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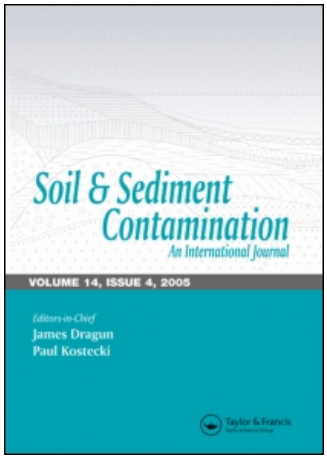

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In Situ Chemical Reduction (ISCR) Technologies: Significance of Low Eh Reactions

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In Situ Chemical Reduction (ISCR) Technologies: Significance of Low Eh Reactions

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Zero valent iron (ZVI; Fe(0)) has been successfully employed for the transformation and subsequent detoxification of a wide range of environmental contaminants, including chlorinated organics, heavy metals, nitroaromatics and, to some degree, perchlorate. The combined use of ZVI plus controlled release carbon has been shown to generate environmental conditions defined herein as in situ *chemical reduction (ISCR) that facilitate the microbiological, chemical and/or physical destruction of various contaminants. In this context, the salient features of ISCR are: (i) its low redox potential; and (ii) its propensity to produce* H_2*. In this paper we discuss the thermodynamics of these characteristics (with special emphasis on ZVI reactions) and provide representative case studies documenting the safe and effective use of ISCR technology to rapidly remove halogenated organics from impacted subsurface environments.*

Keywords Zero valent iron, in situ chemical reduction, reductive dechlorination, groundwater, carbon tetrachloride, permeable reactive barrier, EHC, chlorinated organics, redox potential

Introduction

As used herein, ISCR describes the synergistic effect of stimulated biological oxygen consumption (via degradation of added organic carbon sources), direct chemical reduction with reduced metals, and the corresponding enhanced thermodynamic decomposition reactions that are realized at the lowered redox (Eh) conditions. These combined effects are therefore characteristic for technologies that combine controlled-release carbon plus ZVI or another reduced metal, e.g. Zn(0) (Seech *et al*., 1995 and 2000) or other reducing agents (Szecsody *et al*., 2004) such as dithionite (Nzegung *et al*., 2001). Following placement of ISCR reagents into the subsurface environment, a number of physical, chemical and microbiological processes combine to create very strong (*e.g*., Eh < -550 mV) reducing

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conditions *in situ* that stimulate rapid and complete dechlorination of organic solvents and other recalcitrant compounds:

1. biological reduction/consumption of oxygen and other electron acceptors like, e.g., nitrate and sulfate (via the biological oxygen demand generated by the addition of complex organic carbon);
2. (in)direct chemical reduction via reduced metals either via (direct) chemical reduction of the oxidized pollutants or (indirectly) via the formation of hydrogen, which is used by bacteria as the electron donor (Scherer *et al*., 2000); and
3. direct chemical oxidation via *beta*-elimination reactions and additional oxygen scavenging and reduced Eh via ZVI oxidation/reduction reactions.

Mineralization of halogenated organic compounds occurs via a combination of chemically induced hydrogenolysis, *beta*-elimination, and biological sequential reductive dehalogenation reactions. As such, the accumulation of conventional catabolic intermediates is not observed, and ISCR reactions are more effective toward compounds resistant to individual processes. It is also possible, however, that unique, yet to be identified genes are expressed by dehalogenating microorganisms under these extreme physical conditions, and that such genes produce enzymes that catalyze these reactions (analogous to the synthesis of unique biomolecules under different physical conditions such as pressure and temperature). Studies aimed at evaluating this hypothesis seem warranted.

In any case, degradation routes are kinetically determined, and the type of catalyst and the presence of reactive ZVI surfaces will play important roles in these removal processes. The fermentation of the organic component present in the ISCR reagents liberates various organic acids and reduces naturally occurring reactive metals. This counters the production of hydroxyl ions resulting from the ZVI corrosion process, leading to more reactive ZVI surfaces. The importance of this "buffering capacity" will be discussed here and compared to various other induced anaerobic approaches that employ various carbon sources without the added benefit of ZVI.

It is also noteworthy that under ISCR conditions, the valence state of various inorganic compounds (*e.g*., heavy metals such as chromium(VI)) get reduced, which allows these materials to participate in various sorption and precipitation reactions. In the presence of ZVI and other elements such as sulfur, metals such as arsenic, lead and mercury can also be effectively immobilized *in situ* under ISCR conditions. The primary mechanism of removal is hypothesized to consist of the precipitation and co-precipitation of with iron/sulfur compounds. For example, arsenic is associated with the reduction of sulfate to form stable arsenopyrite (Craw *et al*., 2003; US EPA, 2000) thereby transferring it from the aqueous phase to the solid phase.

Redox Potentials in the Environment

Redox potentials are used to rationalize the sequence in which electron acceptors are used in mature natural environments and to indicate the oxidation state of the system (Zehnder and Stumm, 1988). Redox potentials in the environment normally range between −300 mV and + 600 mV. Redox potentials reported at iron permeable reactive barrier sites with typical groundwater chemical compositions range from −300 mV to −500 mV (*e.g*.: O'Hannesin and Gillham, 1998; Vogan *et al*., 1999; Wilkin *et al*., 2003; Warner *et al*., 2005). Conceptually this implies a high rate of electron production as a result of Fe(0) corrosion.

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Measuring Redox Potentials

Measuring redox potentials is fairly straightforward, but interpretation of the data is challenging. This is due to the fundamental difficulty that redox reactions in the environment are not in internal equilibrium among themselves, because the rates of the redox reactions are very low. This was pointed out more than 20 years ago in a seminal paper in *Science* published by Lindberg and Runnells (1984), and the situation has not improved since. Thus researchers are looking for other ways to delineate the redox conditions of a certain environment. One successful approach is to classify redox settings based on the terminal electron-accepting process that is most likely occurring. This is done by measuring the presence (or absence) of the various compounds that can potentially serve as electron acceptors in the environment (e.g. O_2, Fe^{3+}, MnO_2, NO_3^-, SO_4^{2-}, HCO_3^-) and (ideally) their reduced counterparts (Fe^{2+}, Mn^{2+}, NH_4^+, HS^-, CH_4). Lovley and Goodwin (1988) went one step further and proposed to use the *in situ* hydrogen (H_2) concentration as an indicator of the redox conditions of that particular environment, because each terminal electron acceptor supports a characteristic hydrogen concentration. This approach may work for distinctions between, e.g., sulfate reducing and methanogenic conditions, but is less well suited to delineate the occurrence of dechlorination because, despite some indication otherwise, there is no hydrogen concentration that is characteristic for halorespiration. Also, chlorinated compounds in general are not widely present as natural electron acceptors, especially not in the concentrations found at many contaminated sites. Moreover, frequently only part of the flow of electrons is towards the halogenated electron-acceptor with the remainder flowing to, e.g., sulfate (sulfate reduction) or bicarbonate (methanogenesis). Another possibility for redox measurement that is actively explored is the application of colored redox indicators immobilized on affinity beads or thin membrane films (Jones and Ingle, 2005). Recently, microbial characteristics as measured with the tools of modern molecular biology methods have also been proposed as a proxy for redox characteristics of an environment (Ludvigsen *et al*., 1999; Röling *et al*., 2001; Tian *et al*., 2005). The state of the art still is that measuring redox characteristics in/of the environment is as much an art as a science.

Redox Potentials and Gibbs Free Energies

Given the above problems, but also for other reasons, many environmental microbiologists prefer the use of Gibbs free energy values over the use of redox potentials as an indication of what microbial processes are likely to occur in a certain environment. Redox potential and Gibbs free energy change are two sides of the same thermodynamic coin: $\Delta G^{o\prime} = -nF\Delta E^{o\prime}$. In environmental microbiology we prefer the Gibbs free energy line of reasoning because of its intuitive logic: ΔG values < 0 imply exergonic reactions and ΔG values > 0 imply endergonic reactions. ΔE values, on the other hand, denote a potential difference between two redox couples, but in the literature frequently only one of these couples is addressed, leaving the non-expert guessing about the exact implications. Furthermore, usually in evaluating the redox chemistry of reactions we assume reversibility of the reactions. Often, however, the back reaction is not occurring (Schwarzenbach *et al*., 1993).

Gibbs Free Energies and Redox Potentials of Reductive Dehalogenation

Gibbs free energy values are used to rationalize the role of halogenated compounds as electron acceptors in anaerobic environments and the ability of microbes to use these electron acceptors to obtain energy for growth (Dolfing and Tiedje, 1987; Dolfing and Harrison, 1992;

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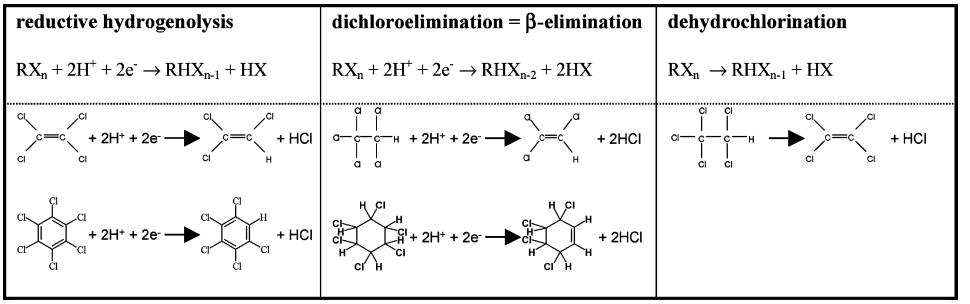

Figure 1. Examples of (reductive) dechlorination redox reactions occurring under anaerobic conditions (after van Eekert and Schraa, 2001).

Dolfing and Janssen, 1994). Furthermore, ΔG values are used to improve our kinetic models (*e.g.* Fennel and Gossett, 1998), as term to delineate thresholds for hydrogen metabolism, and help in discriminating between true halorespiration and reductive dehalogenation as a co-metabolic process (Löffler *et al.*, 1999).

Under standard conditions (pH = 7, 25°C, concentrations of all solutes at 1 M) reductive hydrogenolysis of organic compounds (Figure 1) is an exergonic process. This is true for both aromatic and aliphatic organics, and also for environmentally more realistic conditions (lower concentrations) (Dolfing, 2003). Values for the change in Gibbs free energy values for the reductive dechlorination of various classes of halogenated compounds range between 100 and 180 kJ/mol, i.e. they are comparable for values for reduction of nitrate to nitrite or ammonium. The calculations are made for hydrogen as electron donor at a partial pressure of 1 atm. (100 kPa). In the environment hydrogen is the only electron donor used by dechlorinating bacteria. In sulfate reducing and methanogenic environments hydrogen concentrations range between 1 and 100 nM. Under those conditions reductive dechlorination is still exergonic. There are no thermodynamic limitations, *i.e.* there are no *thermodynamic* reasons why reductive dechlorination should not proceed in those redox environments.

So why do these compounds often persist as contaminants under these environmental conditions, and what can ISCR technology do to stimulate the degradation reactions? Table 1 lists the standard redox potentials of a series of halogenated compounds. The standard in this case is for partial pressures of 1 atm., pH 7, and a chloride concentration of 1 mM. Use of other standard conditions, *viz.* 1 molar solutions, would not change these values appreciably. In the previous sentence we have used the phrase redox potentials of halogenated compounds. It should be noticed, however, that this is a rather loose use of the terminology, as it concerns redox couples rather than compounds. This distinction is not merely semantic or trivial. In many cases a compound can be dehalogenated via different mechanisms (Figure 1): reductive dehalogenation versus dichloroelimination for example. These different reactions lead to different products and different redox potentials. Similarly, dechlorination of hexachlorobenzene to benzene has a different redox potential than dechlorination of hexachlorobenzene to pentachlorobenzene. Thus it is not immediately clear what the redox potential of hexachlorobenzene *per se* is.

Zero Valent Iron as a Source of Reducing Equivalents for Chemical and Biological Ractions

From a thermodynamic point of view ZVI (Fe(0) is an excellent source of reducing equivalents (electrons) for, *e.g.*, microbiological reductive dechlorination. In theory these electrons

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Table 1
Gibbs free energy changes and standard reduction potentials at 25°C and pH 7 of selected organic and inorganic redox couples[a]

Electron Acceptor	Half-reaction of reductive transformations		$\Delta G^{o\prime}$ (kJ/electron)	$E^{o\prime}$ (mV)
Pd^{2+}	**$Pd^{2+} + 2e^-$**	**$\rightarrow$ Pd(0)**	**−88.3**	**915**
1,1,2-TCA	$CHCl_2\text{-}CH_2Cl + 2e^-$	$\rightarrow C_2H_3Cl + 2Cl^-$	−79.8	827
O_2	**$O_2 + 4H^+ + 4e^-$**	**$\rightarrow 2H_2O$**	**−78.7**	**816**
1,2-DCA	$CH_2Cl\text{-}CH_2Cl + 2e^-$	$\rightarrow C_2H_4 + 2Cl^-$	−71.3	738
Fe^{3+}	**$Fe^{3+} + e^-$**	**$\rightarrow Fe^{2+}$**	**−74.4**	**771**
CT	$CCl_4 + H^+ + 2e^-$	$\rightarrow CHCl_3 + Cl^-$	−65.0	673
MnO_2	**$MnO_2 + HCO_3^- + 3H^+ + 2e^-$**	**$\rightarrow MnCO_3 + 4H_2O$**	**−58.9**	**610**
PCE	$C_2Cl_4 + H^+ + 2e^-$	$\rightarrow C_2HCl_3 + Cl^-$	−55.4	574
1,1,1-TCA	$CCl_3\text{-}CH_3 + H^+ + 2e^-$	$\rightarrow CHCl_2\text{-}CH_3 + Cl^-$	−54.1	561
CF	$CHCl_3 + H^+ + 2e^-$	$\rightarrow CH_2Cl_2 + Cl^-$	−54.1	560
TCE	$C_2HCl_3 + H^+ + 2e^-$	$\rightarrow C_2H_2Cl_2 + Cl^-$	−53.1 to −50.9[b]	550 to 527[b]
1,1,2-TCA	$CHCl_2\text{-}CH_2Cl + H^+ + 2e^-$	$\rightarrow C_2H_4Cl_2 + Cl^-$	−51.9 to −49.8[c]	538 to 516[c]
DCM	$CH_2Cl_2 + H^+ + 2e^-$	$\rightarrow CH_3Cl + Cl^-$	−47.6	493
CM	$CH_3Cl + H^+ + 2e^-$	$\rightarrow CH_4 + Cl^-$	-44.8	464
CA	$C_2H_5Cl + H^+ + 2e^-$	$\rightarrow C_2H_6$	$+ Cl^-$	−44.6
VC	$C_2H_3Cl + H^+ + 2e^-$	$\rightarrow C_2H_4 + Cl^-$	−43.4	450
NO_3^-	**$NO_3^- + 2H^+ + 2e^-$**	**$\rightarrow NO_2^- + H_2O$**	−41.7	432
DCE	$C_2H_2Cl_2 + H^+ + 2e^-$	$\rightarrow C_2H_3Cl + Cl^-$	−40.6 to −38.3[b]	420 to 397[b]
1,1-DCA	$C_2H_4Cl_2 + H^+ + 2e^-$	$\rightarrow C_2H_5Cl + Cl^-$	−38.3	397
1,2-DCA	$CH_2Cl\text{-}CH_2Cl + H^+ + 2e^-$	$\rightarrow C_2H_5Cl + Cl^-$	−36.2	375
$Fe(OH)_3$	**$Fe(OH)_3 + 3H^+ + e^-$**	**$\rightarrow Fe^{2+} + 3H_2O$**	**−11.4**	**118**
SO_4^{2-}	**$SO_4^{2-} + 9H^+ + 8e^-$**	**$\rightarrow HS^- + 4H_2O$**	**+20.9**	**−217**
HCO_3^-	**$HCO_3^- + 9H^+ + 8e^-$**	**$\rightarrow CH_4 + 3H_2O$**	**+ 23.0**	**−238**
Ni^{2+}	**$Ni^{2+} + 2e^-$**	**$\rightarrow$ Ni(0)**	**+27.0**	**−280**
proton (pH 7)	**$2H^+ + 2e^-$**	**$\rightarrow H_2$**	**+40.5**	**−420**
Fe^{2+}	**$Fe^{2+} + 2e^-$**	**$\rightarrow$ Fe(0)**	**+42.5**	**−440**
Ti-citrate	**Ti^{4+}. citrate $+ e^-$**	**$\rightarrow$ Ti^{3+}.citrate**	**+46.3**	**−480**
Zn^{2+}	**$Zn^{2+} + 2e^-$**	**$\rightarrow$ Zn(0)**	**+73.6**	**−763**
Al^{3+}	**$Al^{3+} + 3e^-$**	**$\rightarrow$ Al(0)**	**+160.4**	**−1662**

[a]Calculated on the basis of data from Bard *et al*. (1985), Zehnder and Wuhrmann (1976), Dolfing and Harrison (1992), Dolfing and Janssen (1994) and Dolfing (2003), for $[Cl^-] = 1$ mM.
[b]Depending on the isomer formed or dechlorinated (i.e. *cis*- $C_2H_2Cl_2$, *trans*- $C_2H_2Cl_2$, or 1,1-$C_2H_2Cl_2$).
[c]Depending on the isomer formed (i.e. 1,1-$C_2H_4Cl_2$, or 1,2- $C_2H_4Cl_2$).

can be transferred both directly and indirectly via e.g. hydrogen:

$$Fe(0) + 2H^+ \rightarrow Fe^{2+} + H_2 \qquad (\Delta G^{o\prime} = -5.0 \text{ kJ}; E^{o\prime} = 0.440 \text{ V})$$

The equilibrium of this anaerobic oxidation reaction is strongly to the right. This implies that the hydrogen concentration in the proximity of the iron surface is expected to be high from a thermodynamic point of view. Dechlorinating organisms residing in the proximity of Fe(0) particles thus may have two options (provided the increased pH does not inhibit the microbial activity): (i) directly tapping electrons from ZVI via a mechanism that shows resemblance to the nanowires observed by Reguera *et al*. (2005) for iron reduction by *Geobacter sulfurreducens*; or (ii) using the high concentrations of hydrogen. This may

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have a beneficial effect on the combined chemical and microbiological transformation of the target chlorinated compounds in the presence of a zero-valent metal. This was demonstrated by Rosenthal *et al*. (2004) as the presence of *Dehalococcoides* spp., a known PCE degrader, led to a more extensive and rapid dechlorination of PCE in the presence of ZVI. Fe(0) served as a direct electron donor for the microorganisms. The dechlorination by *Dehalococcoides* sp. with ZVI as the sole electron donor was more rapid compared to the dechlorination with H_2 as the electron donor.

Dissimilatory iron reducing bacteria (DIRB) have another way of stimulating the removal of chlorinated compounds in the presence of ZVI. Ferrous iron formed during the anaerobic oxidation can serve as electron donor for the reductive dechlorination of, *e.g*., CCl_4 (Gerlach *et al*., 2000). DIRB will reduce the ferric to ferrous provided a suitable electron donor is present. The potential of ferrous iron to serve as the electron donor (E'^{o} 0.771 V) is, however, limited to compounds like tetrachloromethane that are relatively easily reduced.

The extreme conditions, in terms of the readily available electrons, are part of the explanation why ISCR technology generally results in complete dehalogenation of chlorinated compounds without transient accumulation of partially dechlorinated intermediates. Moreover, the complex organic material provided in the ISCR technology is *in situ* degraded to acetate and hydrogen by the native microorganisms and thus serves as an indirect source of hydrogen for the dechlorinating organisms.

Relationship Between Redox Potential and Dechlorination

Actual measurements have shown that dechlorination reactions proceed faster at lower (more negative) redox potentials. As indicated above, this makes sense from a conceptual point of view. A negative redox potential implies a high electron pressure, i.e. a strong pressure on the halogenated compounds to fulfill their role as electron acceptor. In practice, however, a low redox potential does not automatically imply that the dechlorination reaction will proceed. We have tried to obtain microbiological reductive dechlorination of chlorobenzene with titanium(III) citrate but observed no appreciable dechlorination, under conditions that were virtually identical to those applied by Olivas *et al*. (2002). Thus a low redox potential is helpful, but does not guarantee dechlorination at environmentally relevant time scales because in these cases other factors like chemical stability of a compound start to play a more important role. In general it is believed that lower chlorinated compounds are more easily converted via oxidative pathways, thus under aerobic conditions (Vogel *et al*., 1987). Nevertheless it is possible that reductive dechlorination of chlorobenzene could have been achieved with even lower (more negative) redox potentials in the presence of other (zero valent) metals. Other frequently used zero valent metals have lower E^{o}' compared to the Ti(III)/Ti(IV) couple (Table 1). The redox potential (E^{o}') of these metals like Zn(0) or Al(0) (Bard *et al*., 1985) could generate enough electron donating potential to stimulate reductive dechlorination of lower chlorinated compounds. Unfortunately, the metal ions that are generated in these reactions often are toxic for (dechlorinating) bacteria. Thus, for such a degradation route one would have to rely entirely on chemical transformations.

Dehalogenation Pathways in the Presence of Zero Valent Iron

So far a wide variety of chlorinated (and other) compounds were found to be dehalogenated in the presence of ZVI or other zero valent metals (Scherer *et al*., 2000). Recently, even debromination of PBDEs with Fe(0) was observed (Keum and Li, 2005). Each group of

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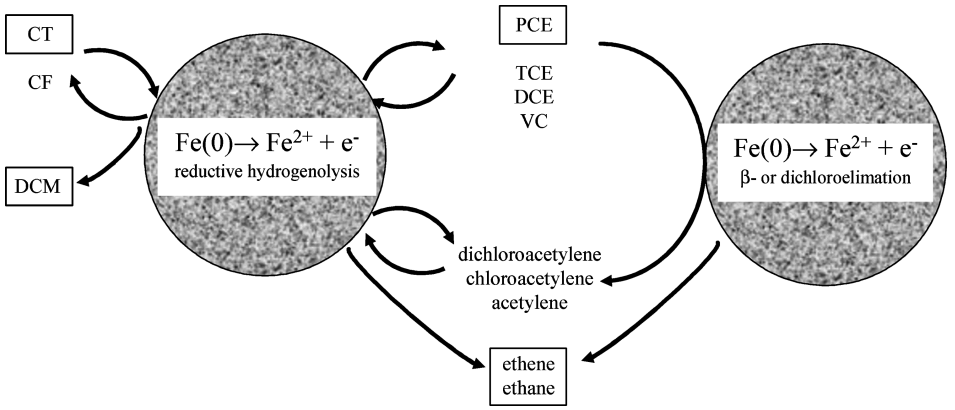

Figure 2. Dechlorination of chloromethanes and chloroethenes by ZVI; Fe(0).

compounds shows its own degradation pathway sometimes combining different dechlorination reactions (Figure 2).

The influence of the presence of dechlorinating microorganisms will not be discussed in more detail (except the two examples mentioned above). Microorganisms are able to adapt to their environment, thus accumulation of an intermediate of chemical dechlorination may lead to the development of a microbial population *in situ* that is able to grow on this intermediate. Whether the presence of the appropriate microorganisms can be ensured through bioaugmentation is depending on the conditions *in situ*.

Redox Properties and Reaction Rates

Reaction rates in the presence of zero valent metals are highly influenced by the nature of the metal. Supplier, purity and size seem to have a large effect on the dechlorination effect. *E.g.*, the half-life of TCE with granular iron was around 10 times lower than powdered ZVI (Cheng and Wu, 2000). However, for Zn(0), which had a degradation capacity that was 10 times higher than ZVI, this effect was not observed. Applying bimetallic systems with either Ni^0 or Pd further enhanced dechlorination via regeneration of the ferrous iron. Nevertheless, stimulation via direct dechlorination by, *e.g.*, Pd(0) was not excluded.

Metals with a more negative $E^{o'}$ may render a more efficient dechlorination but the results found are not equivocal, because the pathway observed with other metals may differ from those observed with Fe(0). Reduction reactions often involve the transfer of 1 or 2 electrons. For most groups of contaminants the transfer of the first electron to the halogenated compound is the rate-limiting step. The application of zero valent metals, reduces the redox potential *in situ* to such extreme values that every oxidized compound is easily reduced. In general higher chlorinated compounds are more easily reduced than lower chlorinated compounds, as was shown for chlorophenol dechlorination by Zn(0) (Kim and Carraway, 2003). The exception to this rule may be the chloroethenes as is described below. There is, however, no consensus on the effect of the redox potential on the reaction rates. Arnold *et al.* (1999) found a straightforward relation between the one-electron reduction potential of chloroethanes and the rate constants in the presence of Zn(0). The same was more or less observed for chloromethanes, chloroethanes, chloroethenes, and chloropropanes in another study with Fe(0) (Scherer *et al.*, 1998). In contrast, others (Li and Farrell, 2001; Arnold

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and Roberts, 2000) conclude that TCE dechlorination by Fe(0) is not only controlled by the one-electron transfer, but also by other chemical dependent factors, like chemisorption.

Particle size is another factor that can have an effect on the redox properties of iron. Trolard and Tardy (1987) have presented a description indicating that the Gibbs free energy of formation (G_f^o) values of goethite (−488.6 kJ/mol) and hematite (−742.7 kJ/mol) increase with 0.156/d and 0.140/d, respectively, where d is the diameter of the particles in μm. In ISCR technology the particle size of Fe(0) ranges between 5 and 45 μm. We are not aware of a similar description for Fe(0), but if we assume that the relationship is quantitatively similar for Fe(0) the effect of particle size on G_f^o and hence on E^o of ZVI as applied in ISCR technology is negligible. On the other hand, it is conceivable that the surface of the particles is far from smooth, and that this affects the local redox conditions.

Case Study

Groundwater at a site in the midwestern USA was impacted with carbon tetrachloride (CT) at concentrations as high as 4,000 μg/L (or ppb). The CT source area is elusive, but impacts are likely the result of using CT as fumigant pesticide in the grain silos on the site. There is a complex geologic history in the study area, which resulted in a mix of interbedded sand, gravel, clay and silt. Two primary saturated sand units have been identified, generally named as the upper and lower saturated sand units. The groundwater table is encountered at approximately 7 m below ground surface (bgs); CT and related impacts are present in the sand aquifer at depths of approximately 9 to 14 m bgs. The resulting CT plume extends about 1000 m downgradient being transported along the topography of the bedrock surface within the higher permeability, sand aquifer.

In March 2005, a total of 22,000 kg of ISCR reagent (EHC; www.adventusgroup.com) was injected into a 82 m long permeable reactive barrier (PRB; see www.eti.ca). The PRB was located at a distance of about 150 m downgradient of the suspected source area and extended across the width of the CT plume. The ISCR reagent was applied at a rate of approximately 1% to soil mass into the saturated sand units. The ISCR reagent was supplied as a dry powder in 23-kg bags and mixed with water on site into slurry containing about 40% solids. The slurry was injected at 126 injection points advanced using a direct push technique. Each injection point was spaced three meter apart. The injection was conducted in a manner to avoid placement of a majority of ISCR slurry into the bottom of a given injection point.

The remedial goal was to treat CT to <5 ppb, chloroform (CF) to <100 ppb, dichloromethane (DCM) to <20 ppb and chloromethane (MC) to <5 ppb in monitoring well MW-105, which was located 9 m downgradient of the PRB (which equals 50 to 114 days in terms of groundwater travel time). The first round of performance monitoring was conducted approximately 30 days after the injections and did not show any effects of the ISCR (Figure 3). However, subsequent monitoring in August 2005 (*ca*. 180 days), October 2005 (*ca*. 210 days) January 2006 (*ca*. 300 days), May 2006 (*ca*. 420 days) and August 2006 (*ca*. 510 days post injection), showed continually decreasing trends in the concentration of CT and all monitored organic constituents of interest. By August 2006, CT concentrations had decreased from >1,600 ppb down to <5 ppb (>99% removal). CF concentrations initially increased from 68 ppb to 270 ppb in August 2005, presumably the result of more conventional anaerobic dehalogenation processes via stimulation of indigenous microbes located downgradient of the PRB by the release of volatile fatty acids, hydrogen, ferrous iron and other soluble elements of the ISCR reagents (in the absence of ZVI per se, the ISCR

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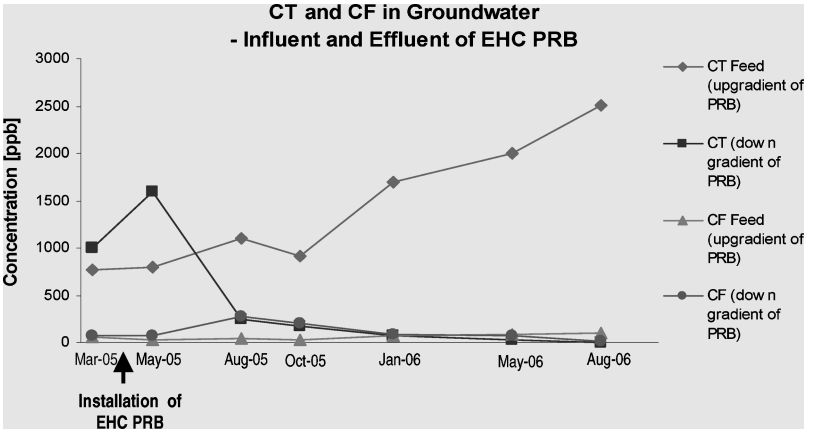

Figure 3. Influence of ISCR PRB on concentrations of CT and CF in groundwater.

processes postulated above are not active). However, by August 2006 the CF concentration downgradient of the PRB had decreased to <11 ppb, which is below background and initial CF concentrations. Simultaneously, DCM remained below the detection limit of 5 ppb, and MC was detected at only 24 ppb in January 2006. Hence, catabolites of conventional reductive dehalogenation processes were not generated or accumulated.

Data from multiple monitoring wells located near the edges of the CT plume showed complete removal of all monitored constituents within 180 days of ISCR treatment (data not shown), and there have been no aberrations in groundwater levels over the course of the monitoring to date that would indicate change in groundwater direction. Hence, lateral by-pass of impacted groundwater was not evident. Likewise, the relative impermeability of the geological unit underlying the PRB, together with the fact that the PRB is permeable, suggested that vertical by-pass (*i.e.*, underflow) was also an unlikely contributor to the removal data observed.

Furthermore, field monitoring data showed that the redox potential (ORP) and dissolved oxygen (DO) concentrations upgradient of the PRB area were generally $> +100$ mV and >1 ppm, respectively; downgradient of the PRB these values were typically < -100 mV and <0.5 ppm, respectively. As of the August 2006 sampling event (*ca.* 510 days of PRB operation), the concentrations of nitrate and sulfate upgradient of the PRB where 4.3 mg/L and 110 mg/L, respectively; downgradient of the PRB these concentrations were <0.05 mg/L and 23 mg/L, respectively. The total organic carbon (TOC) concentration upgradient of the PRB was generally around 2 mg/L, whereas downgradient of the PRB these values have ranged from 10 to >1,000 mg/L. As of the August 2006 sampling event, data suggests that the TOC concentration downgradient of the PRB is trending downward. There are no monitoring points within the PRB itself.

The injections where completed within 10 days at a cost <$90,000 USD. The material cost of using EHC ISCR reagent was $37/ft^2 ($395/m^2) of PRB cross-section (270 ft long × 9.7 ft deep on average), or about $90,000 USD. Using an estimated linear groundwater velocity of 1.8 ft/day (1.6 to 2.2 ft/day estimated) and a porosity of 30%, the PRB is treating an estimated total of 516,000 ft^3 (14,600 m^3) of groundwater per year (270 ft long × 9.7 ft average depth × 365 days × 1.8 ft/day × 30%). With an estimated life of at least 5 years, the PRB is expected to treat a total of 2,580,000 ft^3 (73,000 m^3) of groundwater during its life-time at a product cost of $0.04/ft^3 ($1.32/m^3).

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Conclusions

Enhanced biogeochemical degradation of CT or other organic compounds under ISCR conditions as defined herein is the result of integrated physical, chemical and microbiological processes or other heterogeneous reactions (Amonette *et al.*, 2000). It was beyond the scope of these efforts to delineate the importance or proportional of these independent reactions or processes. It is clear, however, that there is no *a priori* thermodynamic reason why extra low redox conditions as induced by ZVI would stimulate reductive dechlorination of halogenated compounds any better than the redox conditions typical for methanogenic environments. The Gibbs free energy change of these compounds is such that, from a thermodynamic point of view, they are also labile under the hydrogen concentrations prevailing in*e.g.* sulfate reducing and methanogenic conditions. The fact that these compounds often persist under these conditions indicates that the situation is more complex. Thinking along the lines of redox potentials rather than in terms of Gibbs free energy changes, it becomes conceptually clear that a low redox potential translates into a high pressure of electrons and hence a high pressure on the halogenated compounds involved to be reduced. For the organisms involved in degrading those compounds which do not come into direct contact with metal surfaces this implies that there is considerable energy to be gained. This suggests that under ISCR conditions (*i.e.*, <450 mV Eh), microorganisms that can benefit from catalyzing these reactions will proliferate. As suggested by the hydrogen scavenging nanowire scenario referenced above, it is tempting to speculate that organisms similar to *Dehalococcoides* species may develop mechanisms that can harness the (extra) energy more efficiently than the dechlorinating organisms known so far.

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