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The Technical Basis for In Situ Chemical Reduction (ISCR)

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ABSTRACT: In Situ Chemical Reduction (ISCR) is a new and evolving technology based on the convergence of four parallel technical developments, which include (1) the use of zero valent iron for reductive dechlorination, (2) the reductive capabilities of ferrous iron, (3) the abiotic attenuation of chlorinated solvents, and, (4) the treatment of soils with chemical reductants and/or biological processes to enhance or create reactive, reducing zones. While various elements of these developments have been known since the late 1970s, the realization of the consonance and correlations between these four developments has generated a new remedial approach for treating chlorinated solvents—the intentional use of chemically mediated reductive processes to destroy or detoxify chlorinated solvents, ISCR. As a remediation technology, ISCR is in its initial phase of development. The processes involved and the factors which influence or control them are not fully known or understood. The interaction between abiotic and biotic reduction is also not fully understood. Much research still needs to be conducted to continue to develop ISCR as an important remedial process for treating chlorinated solvents.

INTRODUCTION:

The development of In Situ Chemical Reduction (ISCR) is based on four principles. These principles are:

1. All abiotic reductive processes involve a form of reduced metal, typically iron, which can be either zero valent or ferrous (+2) iron.
2. Iron-mediated reductive pathways are, in general, different than those that occur with biologically mediated reduction.
3. Iron-based reductive processes are strongly surface dependent.
4. Iron-mediated reductive processes can be enhanced through the use of chemical reductants and/or biological reduction.

These principles have been based on and derived from parallel technical developments. The following discussion provides an overview of the historical development of these principles and the technical basis of ISCR.

The Use of Reduced Iron. The development of ISCR has been based on the elucidation of reduced iron chemistry. The first aspect of the development of iron-based reductive chemistry was the use of zero valent iron (ZVI). The use of zero valent metals to dechlorinate halo-organics in aqueous streams has been known since the late 1970s (Sweeney, 1980). Sweeney was able to treat a wide range of chlorinated organics including DDT, chlorobenzene, endrin, heptachlor, chloroform and hexachlorocyclopentadiene, with copper-doped iron and aluminum.

This metal-based reductive chemistry was subsequently applied to groundwater treatment with the emplacement of ZVI barriers in the early 1990s (Gillham, 1993; Tratnyek, 1996). While other zero valent metals such as aluminum and magnesium have been used in the laboratory, the focus in groundwater treatment has primarily been on the use of iron (ZVI). By 1995, the U.S. Environmental Protection Agency (EPA) cited 10 demonstration projects for iron barriers, primarily ZVI. (EPA, 1995). One of the barrier systems, however, included the use of sodium dithionite to create an *in situ* reduced iron zone to treat a Cr VI plume.

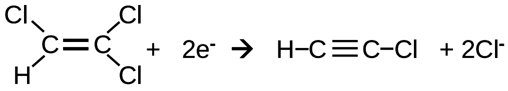
Early in the development of ZVI technology, the potential role of ferrous iron in reductive dechlorination was considered. Ferrous iron, formed by the corrosion (reaction) of ZVI, was thought to also react with chlorinated solvents. (Matheson, 1994, Tratnyek, 2006). Additionally, parallel to the investigation of ferrous iron associated with ZVI technology, other researchers specifically investigated the reductive reactivity of reduced iron minerals such as pyrite and demonstrated that a suspension of pyrite was able to dechlorinate carbon tetrachloride (Kriegman-King, 1994) and reduce DNT (Jiayang, 1996). Additional research has shown that chemically-precipitated ferrous iron is also an active reductant for chlorinated volatile organic compounds (CVOCs) (Brown, 2005b).

The final aspect of iron-based reductive chemistry that serves as a basis for ISCR has been the ambient reactions of naturally occurring, ferrous-containing minerals with chlorinated solvents. In 2002, a plume of cis-1,2-dichloroethene (cis-DCE) was shown to be abiotically degraded by magnetite (Ferrey 2002). The abiotic reduction of .chlorinated solvent by reduced iron minerals is thought to be a major attenuation pathway (Wilson, 2003).

The importance of the role of iron to ISCR is that iron is a commonly occurring element. Iron is the fourth most abundant element in rock formation, comprising, on average, about 5% (by weight) of rocks. This abundancy suggests that ISCR could have broad applicability.

Potential Reductive Pathways. In his investigation of halo-organic reduction in aqueous waste streams**,** Sweeney postulated that a number of probable reductive reactions were involved, including hydrogenolysis, hydrolysis, ring-opening, rearrangement, and condensation, all catalyzed by the zero valent metal (Sweeney, 1980). In 1987, Vogel, Criddle and McCarty postulated a number of two-electron reductive pathways for chlorinated aliphatics including hydrogenolysis, the replacement of a chloride by hydrogen; dihalo-elimination, removal of two adjacent chlorides generating a carbon-carbon bond; and, coupling the removal of two chlorides from two different molecules generating a carbon-carbon bond combining the two molecules (Vogel, 1987). Early publications presaged the diversity and complexity of metal-catalyzed reductive reactions.

The early development of *in situ* metal-based reductive processes did not, however, avail itself of the pioneering work of Vogel and Sweeney. Originally, much of the literature assumed that ZVI reduced chlorinated solvents by sequentially replacing chlorine atoms with hydrogen, the same process as has been observed with the biologically mediated reductive dechlorination. This two-electron reduction is termed hydrogenolysis. With this mechanism, ZVI would convert tetrachloroethene (PCE) to trichloroethene (TCE), TCE to cis-DCE, cis-DCE to vinyl chloride (VC), and VC to ethene. What has been more recently discovered, instead, is that ZVI operates by more diverse mechanisms than just the hydrogenolysis pathway. With PCE, TCE and cis-DCE, a key reductive pathway is postulated to be a β-elimination (dihalo-elimination), wherein two chlorines are removed via a two-electron reduction and the ethene is converted to an acetylene (Arnold, 2000):

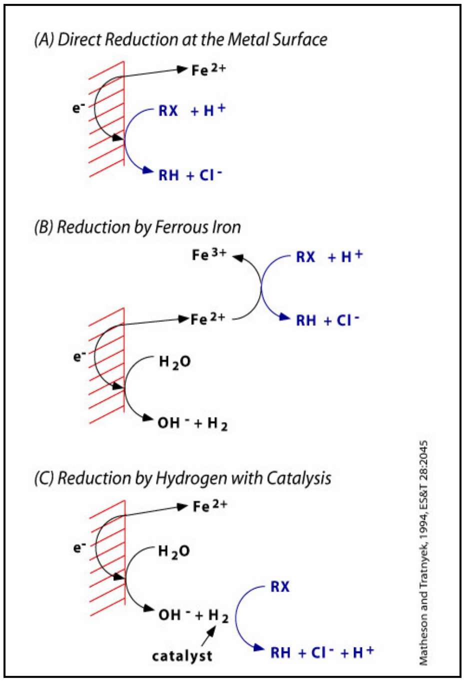


The mechanisms of the reaction of ZVI with chlorinated solvents are quite complex and generate multiple products. Orth and Gillham (Orth, 1996), in a study of the reaction of TCE with ZVI, found that ethene and ethane (in the ratio 2:1) accounted for over 80 percent of the original equivalent TCE mass. The typical daughter products, such as cis-DCE and VC, formed biologically, accounted for only 3 percent of the original TCE mass. Additional byproducts were found including hydrocarbons (C_1 to C_4) such as methane, propene, propane, l-butene, and butane.

Other researchers have found similar mixtures from the reaction of TCE and PCE with ZVI (Campbell, 1997). VC, cis-DCE, 1,1-dichloroethylene, methane, chloroacetylene, acetylene, ethylene, ethane, and $C_{3–5}$ alkenes and alkanes were observed as products.

One of the important discoveries that has been key to the development of ISCR, is the discovery that ferrous iron reacts with chlorinated solvents by mechanisms similar to those observed for ZVI. Chloroacetylenes were observed as products in the reaction of TCE with reduced iron-containing sediments (Szecsody, 2004).

The significance of the diversity of reaction pathways for the iron-based reduction of chlorinated solvents is that toxic byproducts (e.g., VC) do not accumulate with abiotic reduction as is often observed with biologically-mediated reductive dechlorination. The lack of toxic byproducts eliminates some of the concerns that arise with biological reduction.



Matheson and Tratnyek, 1994, ES&T 28:2045

FIGURE 1. ZVI reduction mechanisms.

Surface Catalyzed Reactions. ZVI technology is, by its nature, a surface-based reaction. Much of the technology development for ZVI has focused on understanding the mechanisms of the reaction of chlorinated solvents with ZVI surfaces. Tratnyek and Matheson postulated three possible reductive mechanisms (Matheson, 1994) pictured in Figure 1. These pathways included direct reduction, electron shunting through ferrous iron, and reduction by production and reaction of hydrogen.

In reviewing the mechanisms of ZVI reduction, Richards postulates that the reduction of chloroethenes is a six-electron transfer with the ethene being bound to the metal surface by "strong chloroethene-iron pi bond…" which "prevents desorption until dechlorination is complete…" (Richards, 1998)

Subsequent work on reductive reactions with ferrous iron have shown that the reactions are also surface catalyzed (Elsner, 2002). The reactivity of bound ferrous iron was found to be a function of the surface area and of the geochemical conditions. In general, iron sulfides and oxides were the most reactive reduced minerals.

Recent studies have suggested that soluble ferrous iron has a role in the activity of ferrous iron minerals. The reduction of *cis*-DCE with magnetite was enhanced with the addition of soluble ferrous iron (Ferrey, 2004). The role of the soluble ferrous iron is unknown but may be related to the regeneration of active sites (Scherer, 2005).

The significance of the role of surface reactions in ISCR has both positive and negative aspects. On a positive note, ISCR lends itself to creating effective barriers to contain, control and treat chlorinated solvent plumes. The negative aspect is that ISCR may not be easily applicable for treating source areas as it would have a limit to the turnover of chlorinated solvents tied to the indigenous iron content.

Enhancement of Reductive Pathways. Abiotic reductive processes can be enhanced by two methods. First, the amount of reduced iron available can be increased to increase the rate of reduction observed. The amount of reduced iron can be increased by chemical or by biological means. Second, the reducing ability of the iron can be enhanced by coupling it with other chemical reductants or with biological reduction.

Researchers at Battelle Pacific Northwest National Laboratory (PNNL) developed an *in situ* technology using sodium dithionite to reduce iron in a ferroaluminosilicate, creating a reactive reduced zone (Szecsody, 2000). The technology was originally developed to treat Chromium VI, but was later found to reduce TCE effectively. The TCE was degraded by reductive elimination yielding acetylenes and ethylene. This technology demonstrated that the activity of reduced iron could be artificially stimulated or increased by the injection of a non-metallic, soluble chemical reductant.

Biological reduction also can create reduced minerals that are active dechlorinating agents. Lee used sulfate-reducing conditions to produce ferrous sulfide by injecting sulfate with an edible oil substrate (Lee, 2002) Ferrous sulfide was produced through bacterial action. TCE was rapidly degraded to ethene without significant production of *cis*-DCE or vinyl chloride. While acetylene was not detected, the depletion of TCE without the production of *cis*-DCE or vinyl chloride was taken as proof of abiotic degradation.

A second enhancement of iron-based reduction is coupling iron with other reductants or reductive processes. The rate of reduction of a variety of CVOCs by ZVI and by ferrous iron was significantly increased by the addition of sodium dithionite (Brown 2004). The increase in activity was proportional to the ratio of dithionite to iron; the more dithionite added, the greater the rate increase.

Biological enhancement is also feasible. Adventus has developed a unique product (EHC™) which combines a controlled release carbon with ZVI. As shown in Figure 2, this combination results in a very low reduction potential. The carbon creates anaerobic conditions, which enhances the reducing ability of the ZVI resulting in a very low potential. At this potential, chlorinated solvents are chemically unstable (Mueller, 2004). TCE degrades under these conditions without the production of chlorinated daughter products (Seech, 1995).

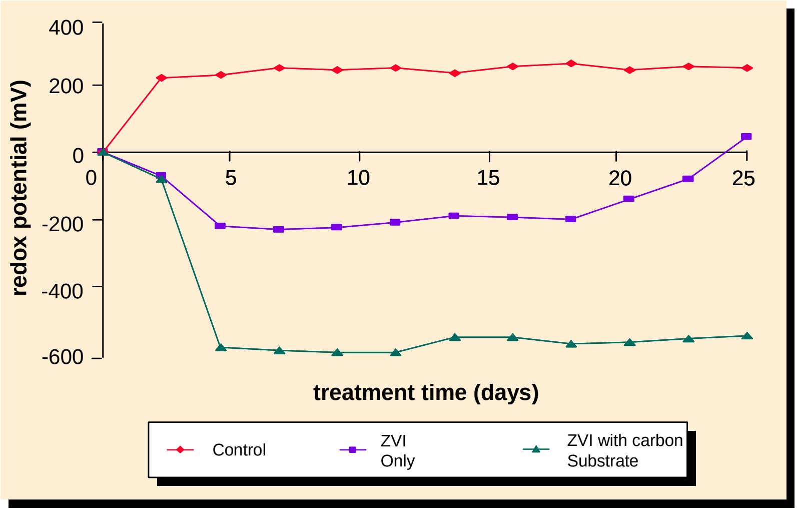


FIGURE 2. Reduction potential for combined ZVI and carbon (adventus).

The significance of these enhancements is that increasing the amount of reduced iron or enhancing the reducing conditions increases the effectiveness of ISCR. This observation means that ISCR has the potential to be an engineered system. Also, the ability to increase and enhance reduced iron by the addition of a soluble chemical reductant or by biologically creating anaerobic conditions suggests that ISCR may become an easier-to-apply technology than the emplacement of ZVI barriers, which have been, to date, the more commonly applied ISCR technology. ZVI is an effective technology, but it is often difficult and expensive to apply.

RESEARCH NEEDS

Even though some of its bases (e.g., ZVI) have been in place for over twenty years, ISCR is a relatively new technology. As a result, a number of research areas need to be investigated to further its development. These areas include:

1. Identifying the factors that control the reactivity of reduced iron minerals. Recent work has seen a difference in reactivity between natural, chemically produced and biologically produced iron minerals (Scherer, 2005). Soluble iron and pH may be factors in controlling reactivity.
2. Investigating the interaction between biological reduction and abiotic reduction. Considering the range of natural and applied conditions that have been studied, the two processes may be synergistic, antagonistic, or non-interactive.
3. Investigating the interaction of soluble reductants with reduced iron minerals by (1) examining the efficacy of different reductants and (2) determining the effect of residual reductant. Some studies suggest that residual reductant is beneficial [Brown, 2005 (1)]; others suggest it is detrimental (Szecsody, 2000).

CONCLUSION

When the above developments are examined together, a number of conclusions can be drawn concerning the reactivity and effectiveness of ISCR:

- Reduced iron minerals can effectively degrade chlorinated solvents including chloroethenes (PCE, TCE), chloroethanes (TCA, DCA) and chloromethanes (carbon tetrachloride),
- Reduced iron minerals react by generally the same pathways as ZVI to dechlorinate chlorinated solvents.
- A number of iron minerals such as pyrites, green rust (mixed Fe (II) and Fe (III) oxides and hydroxides), and magnetite are active reductants,
- Oxidized iron minerals can be reduced *in situ* by the application of a chemical reductant or by biological reduction generating active reduction zones.

ISCR, though still in its initial phase of development, has the promise of becoming a key remediation technology. It complements some of the existing remedial systems such as BRD (biological reductive dechlorination) and ISCO. Table 1 provides a comparison of these three remedial technologies.

TABLE 1. Technology comparison.

	ISCR	ISCO	BRD
Preferred Geological/Geochemical Conditions	Available iron mineralogy	Low FOC (Permanganate), Low Mn/Fe (Peroxide), Low Mn (Persulfate)	Available natural organics, Low-Moderate Fe/Mn (competitive metabolism)
Applicability to Chloroethenes – PCE, TCE, cis-DCE	Very good for PCE/TCE, slow for cis-DCE	Very good for all	Good for PCE/TCE, sometimes stalls @ DCE or VC
Vinyl chloride production/reactivity	Little accumulation	Does not form VC. Reactive to VC	Accumulation possible
Applicability to Chlorethanes – TCA; 1,1-DCA; 1,2-DCA	Treats TCA, 1,1-DCA, 1,2-DCA	Limited applicability, Requires very aggressive systems for Chloroethanes	Generally reactive but accumulates chloroethane
Applicability to Chloromethanes – CT, CF, DCM	Treats CT, CF. Little accumulation of DCM	Limited applicability, Requires aggressive systems for Chloromethanes, such as heated persulfate	Generally reactive but accumulates DCM
Relative rate of treatment	Slow to moderate	Fast	Slow to moderate
Key factors limiting success	Available iron, reduced iron	Stability/consumption of oxidant	Requisite bacteria, available carbon source
Compatibility with MNA	Very good	No effect on down gradient MNA. Limits MNA in treatment area	Very good if right bacteria present and properly maintained with multiple additions of agents (substrate)
Effect of Redox conditions	Works best in anoxic to anaerobic conditions. Not compatible with highly aerobic conditions	Works best in oxic to aerobic conditions. Not compatible with highly reducing conditions	Works best in anoxic to anaerobic conditions. Not compatible with highly aerobic conditions

Agents needed	Reducing agent, available iron	Oxidant and in some cases a reaction catalyst (persulfate, peroxide)	Carbon source, inoculum, nutrients
Residual effect after agent spent	Reduced iron continues activity. No reapplication may be needed	No reaction without oxidant. Reapplication may be required to meet goals	No degradation without carbon. Reapplication required to meet goals

As can be seen from this table, each of these remedial technologies has its own niche. None is universally applicable. Proper use of ISCR requires understanding its capabilities and limitations.

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