

Date: July 2009
To: Remediation Practitioners and Professional Colleagues
From: John Vogan – President
Subject: Clarification of ZVI and ISCR™ Biogeochemistry

Recently a colleague passed on a document from a competitor's (Regenesis) web page entitled "Comparative Technology Review – Vegetable Matter/ZVI Blends: Technical Mechanisms and Lack of Performance".

See Appendix (**hotlink:** <http://www.regenesis.com/library/technical%20bulletins/regenox/techreviewvegmatter.zviblends.pdf>)

Like most professional readers of such publications, we understand these are not scientific documents but that they are written mostly by salespeople and, as such, we normally peruse the information - albeit "with a grain of salt" - and let it pass.

However, there are statements in this particular document that indicate a fundamental misunderstanding of basic, freshman-level zero valent iron (ZVI) reaction chemistry along with a fundamental lack of awareness of available field data. As creators of the original *In Situ* Chemical Reduction (ISCR™) technologies consisting of combined organic carbon + ZVI (or other metals), namely EHC® and DARAMEND®, we feel an obligation to address these misleading, erroneous statements and have therefore contrasted herein for your benefit Regenesis' "summary comments" with scientific reality.

1. *"The major pathways for ZVI degradation of chlorinated ethenes are through sequential dechlorination (includes biotic and abiotic)".*

The Regenesis authors are confused as to the nature of ZVI-chlorinated ethene interactions. These reactions are indeed abiotic. Moreover, their use of the term "sequential degradation" indicates a lack of understanding regarding what happens when trichloroethene (TCE), for example, contacts ZVI:

"Generally less than 5-10% of the initial TCE appears as chlorinated degradation products, including the three dichloroethene products (cDCE) and VC". (US EPA, 1998).

"These alternative pathways also could explain why only a small percentage (usually 3 to 5 percent) of the original PCE or TCE is realized as DCE or VC by-product (Gavaskar et al, 1997)".

2. *"Rapid and complete contaminant degradation can occur with ZVI, but only when direct contact is made between contaminants and the iron surface, and only when contact is made over a significant residence time, as in "funnel and gate" – type barriers where contaminants are forced to cross a ZVI filled trench of adequate thickness".*

Of the over 200 ZVI applications of which we are aware, less than 10 involve “funnels and gates”. Moreover, the term “significant residence time” is also misleading. Degradation rates (half-lives) summarized in a variety of 3rd-party guidance documents range from two to ten hours for common chlorinated ethenes, certainly faster than degradation rates which can be achieved with any of the authors’ bioremediation approaches. The design residence times in most field-scale PRBs are on the order of one to three days, not “significant” in view of groundwater flow rates at most sites.

3. *“Injecting micro-scale ZVI has not been shown to be commercially viable due to the high cost of fracturing the material into the subsurface and the inadequate distribution of material – not allowing for direct contact to occur”.*

We recommend the authors to review Chapter 7 of the 2005 ITRC guidance document, which discusses various approaches of ZVI injection for VOC treatment. In particular, one of our injection partners, ARS Technologies Inc. (www.arstechnologies.com) has completed over 30 successful projects using their FeroxTM pneumatic fracturing and injection process, and another 10 injection projects are listed in ETI’s database that use a variety of fracturing and direct injection approaches. There are many, many others. Our experience is that, in contrast to the above statement, a properly designed iron injection is indeed a cost-effective means of achieving significant VOC reduction **without the accumulation of problematic catabolites**.

4. *“Claims made by manufacturers of vegetable matter/ZVI blends of rapid parent compound degradation without generating daughter products are unfounded and viewed by most in the environmental industry as lacking technical credibility”.*

This statement, essentially repeated in Conclusion 5, could easily be construed as “the pot calling the kettle black”, as we know of several instances where a “vegetable matter/iron blend” (*i.e.* our EHC[®] product) has been successfully applied after an injection of a competitor’s aqueous carbon substrate that led to the very build-up of daughter products discussed here. The authors conveniently ignore the numerous case studies readily available in the literature describing successful full-scale field applications of EHC[®] ISCRTM technology. There are over a dozen listed on our website (www.adventusgroup.com). Of course, these applications are subjected to 3rd-party reviews, and have been published in a variety of documents, for example:

- Clean-up of a tetrachloroethene plume at an Oregon drycleaner (<http://www.deq.state.or.us/wrd/r/?p=20107>)
- Clean-up of a carbon tetrachloride plume at an agricultural facility (Molin *et al*, 2008)
- TCE plume remediation using EHC[®] and KB-1[®] (Peale *et al*, 2008)
- *In Situ* chemical reduction of commingled hexavalent chromium and TCE plume (Frain *et al*, 2008)
- EHC for 1,2-DCA and VC (Sandrone *et al*, 2009)

Given the above, one might question whether picking one table out of this fairly robust data set is a fair, technical means of technology evaluation.

OVERVIEW OF EHC® *IN SITU* CHEMICAL REDUCTION (ISCR™) TECHNOLOGY

In situ chemical reduction (ISCR™) describes the combined effect of stimulated biological oxygen consumption (via fermentation of a hydrophilic, complex organic carbon sources), direct chemical reduction with ZVI or other reduced metals, and the corresponding enhanced thermodynamic decomposition reactions that are realized at the lowered redox (Eh) conditions. A number of enhanced reductive dehalogenation (ERD) and other accelerated anaerobic bioremediation technologies exist (*e.g.*, emulsified oils, oils, carbon-based hydrogen release compounds) that purportedly offer similar responses. However, the EHC® substrates are unique in their ability to provide ZVI to thus yield Eh values as low as -600 mV, termed herein ISCR™.

The use of ISCR™ technologies has recognized potential for managing soil and groundwater environments contaminated by chlorinated solvents, pesticides, heavy metals and other constituents of interest (COI). A number of factors have been identified as important variables in remedial design and ISCR™ technology selection. ISCR™ criteria and differentiators include:

1. No reliance on physical, short-term sequestration of targeted compounds as a primary removal mechanism (as is common with [emulsified] oils);
2. No accumulation of often persistent intermediates (such as DCE) as a function of substrate addition (as is common with [emulsified] oils and sources of carbon only);
3. No physical displacement of COIs via substrate addition and water flushing (as is common with [emulsified] oils);
4. No problems associated with aquifer acidification (as is common with [emulsified] oils and sources of carbon only);
5. Will not mobilize arsenic or other heavy metals yielding secondary contaminants (as is common with [emulsified] oils and sources of carbon only);
6. Has been easily applied globally in many lithologies using conventional construction equipment;
7. Environmental longevity (3 to >5 years depending on contaminant mass flux etc.);
8. Applicability to source areas, hot-spot treatment or permeable reactive barriers;
9. Ability to immobilize heavy metals present as co-contaminant;
10. Cost effective at \$2.50/lb (volume discounts apply) and made regionally, globally; and

11. Technology end users and their clients are fully protected from all Patent and related intellectual property legal issues.

In summary, we hope the above serves to clear up the Regenesys' misconceptions regarding ZVI / EHC[®] ISCR[™] biogeochemistry and field application record. We would be happy to provide any of the 3rd-party back-up documentation referenced herein.

Please feel free to contact us with any questions or comments – you will get a timely, thoughtful and technically defensible reply. Thank you for your time and attention.

References

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COMPARATIVE TECHNOLOGY REVIEW

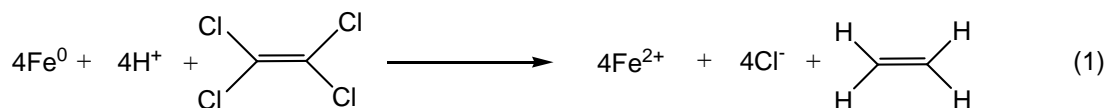
Vegetable Matter/ZVI Blends Technical Mechanisms and Lack of Performance

Introduction

Within the scope of *in-situ* treatment of chlorinated solvents, the primary contaminants encountered are the chlorinated ethenes such as tetrachloroethene (PCE), trichloroethene (TCE), dichloroethene isomers (DCE), and vinyl chloride (VC). Enhanced anaerobic bioremediation has emerged as a premier technology for remediation of these contaminants *in-situ*, where the above compounds are biologically dechlorinated to ethene using a slow-release electron donor such as Hydrogen Release Compound (HRC[®]).¹ While it is much faster acting than monitored natural attenuation (MNA), enhanced bioremediation does require months to years for its full effect to be observed. In favor of faster remediation there is increasing interest in chemical technologies that can directly and rapidly react with contaminants in the subsurface. The relatively oxidized nature of halocarbons, such as the chlorinated ethenes, leads to the prospect of using chemical reductants to break carbon-chlorine bonds and convert contaminants of concern (COCs) to less toxic hydrocarbon products, such as ethene, in a rapid time frame. The prospect of employing reducing agents in remediation has been coined *in-situ* chemical reduction (ISCR).

Zero-Valent Iron (ZVI)

Iron, in the form of oxides and carbonates (e.g. magnetic, hematite, limonite and siderite), is abundant in the earth's crust; however, zero-valent iron (ZVI) is primarily a man-made material. ZVI is commonly used as an ISCR agent. Equation 1 is a simple representation of the reduction of PCE to ethene by ZVI. This representation considers the transformation from Fe⁰ to Fe²⁺ where in practice Fe²⁺ may also oxidize to Fe³⁺.

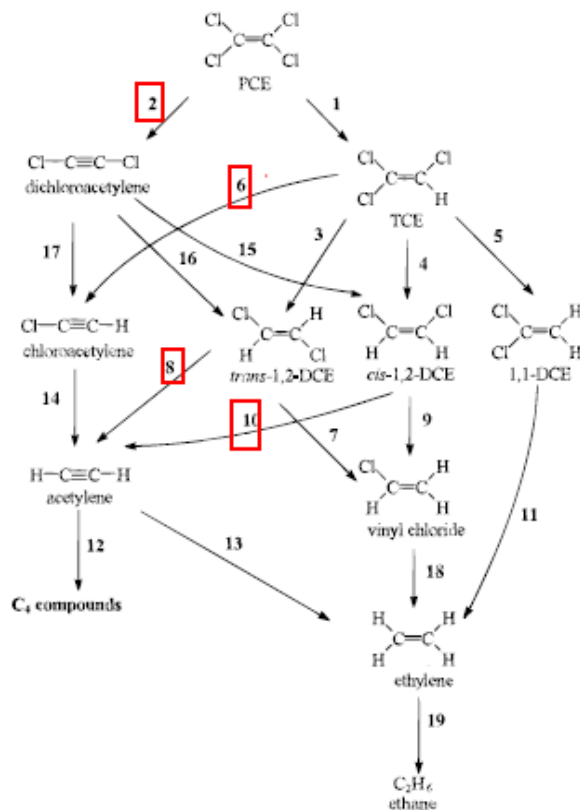


Equation 1. Transformation of PCE to Ethene via ZVI

Mechanistic Details – ZVI

Laboratory studies have shown that iron metal can reduce PCE to ethene; however the mechanisms at work in this process are a matter of debate. Some have reported that the reaction proceeds via β -chloride elimination from iron-vinyl complexes and that PCE degradation proceeds through acetylene intermediates and does not produce much, if any, chlorinated ethylene daughter products.² However, Roberts et al.^{3,4} have shown that chlorinated ethene reduction by zero-valent metals proceeds via

two parallel pathways: hydrogenolysis and reductive β -elimination (see Scheme 1). Field Studies with ZVI have shown that a significant (the majority) of the degradation of chlorinated ethenes is the result of reductive dechlorination. Therefore, the exact mechanistic details of ZVI products, especially when combined with organic material, are not well defined and are probably very site specific.



Scheme 1. Depiction of the Hypothesized Reaction Pathways for Chlorinated Ethenes During Reduction by Fe^0 . The red boxes indicate the β -elimination pathway.

Field Application of ZVI

The use of iron as a reducing agent for treatment of contaminated groundwater is well documented.^{5,6,7} In this form metallic iron is placed into a subsurface trench perpendicular to groundwater flow. The groundwater to be treated is channeled through the trench so as to force the contact of the dissolved halocarbon contaminant directly with the zero valent iron particles (so called “funnel and gate”). Only some 125+ such PRB systems have been installed in the past decade.⁷ The reason more of these systems have not been installed is due to the fact that these installations are very costly to successfully construct relative to enhanced biodegradation systems and the barrier, once installed, only treats the flux of contaminants directly contacting the iron within the trench, leaving the source area and the balance of the plume untreated.

In an attempt to treat an entire contaminant plume, rather than simply putting in a down-gradient barrier, practitioners have tried to directly inject zero-valent iron into the contaminated aquifer matrix. Early attempts employed iron particles sized on the order of micrometers (so-called “micro-scale” iron). Attempts to inject this material using conventional injection techniques such as direct-push equipment quickly proved unsuccessful. It was then recognized that high pressure fracturing techniques were required in order to force the micro-scale iron into the aquifer matrix. This fracturing causes uneven placement of the iron material within the treatment zone as the iron particles are preferentially placed only within the fractures produced. Thus, the only reductive treatment achieved is

that of the contaminant molecules that happen to contact the iron concentrated within the fractures. Under this scenario, the vast volume of the contaminant plume goes untreated.

Vegetable Matter/ZVI Blends

Products are now on the market which are composed of vegetable matter blended with small amounts of micro-scale zero-valent iron. Manufacturers claim that when this material is injected in the subsurface a synergistic effect occurs between the iron and vegetable matter allowing for rapid and complete dechlorination of target contaminants without producing intermediate partially-chlorinated daughter products.⁸ (Daughter products generally associated with reductive dechlorination of PCE include TCE, DCE, and in some cases small concentrations of VC.) Unfortunately, there is no credible documented scientific account of how this vegetable matter/ZVI induced mechanism could occur.

Upon injection of these vegetable matter/ZVI blends, one would expect to see fermentation of the vegetable matter generating hydrogen which, in turn, would stimulate the sequential dehalogenation reaction through the typical daughter product sequence (PCE to TCE to DCE to VC to ethene). This, in fact, is exactly what engineering firms employing these products actually see in the field.

Typical site data is presented in Table 1 (actual data from a field application of a vegetable matter/ZVI blend). Nine months after injection of the material, only 17% to 55% of the parent product was removed. Furthermore, after nine month's time, all expected daughter products were produced in significant quantities including a **1000X increase in vinyl chloride**, a compound rarely seen to accumulate in any significant quantity under typical biological reductive dechlorination conditions such as those generated by HRC[®] and 3-D Microemulsion (3DMe)[™]. This is clear evidence that the vegetable matter/ZVI blend doesn't perform in a more effective manner than biological reductive dechlorination technology and certainly does not eliminate daughter products - quite the opposite is evident!

Table 1: Results of Vegetable Matter/ZVI Blend at a TCE-Impacted Site*

| Well | Time | TCE (ug/L) | DCE (ug/L) | VC (ug/L) | Sum cVOCs (ug/L) | % TCE Removal | % cVOC Removal |
|-------------------------------|-----------|------------|------------|-----------|------------------|---------------|----------------|
| Shallow PRB | Injection | 6,500 | 89,010 | 30 | 95,540 | 99.48 | 33 |
| | +9 mos | 33.5 | 25,839 | 43,300 | 63,756 | | |
| Deep PRB | Injection | 92,900 | 39,497 | 22 | 132,419 | 99.99 | 55 |
| | +9 mos | 62.5 | 43,914 | 15,500 | 59,476 | | |
| Shallow Down-gradient (10 ft) | Injection | 7,990 | 91,624 | 26 | 99,640 | 92 | 35 |
| | +9 mos | 678 | 42,502 | 21,200 | 64,380 | | |
| Deep Down-gradient (10 ft) | Injection | 198,000 | 34,133 | 41 | 232,174 | 81 | 17 |
| | +9 mos | 36,800 | 151,177 | 5,190 | 193,167 | | |

*Reference: www.adventusgroup.com, May 10, 2007- use of EHC[®] (typical vegetable matter/ZVI blend)

The iron in these vegetable matter/ZVI blends does however, make the application of the material to the subsurface very difficult. Application of these materials generally requires high pressure fracturing to apply. This requires specialized fracturing equipment and ultimately places the material within specific fracture planes rather than across the contaminated target zone.

Summary

1. The major pathways for ZVI degradation of chlorinated ethenes are through sequential dechlorination (includes biotic and abiotic);
2. Rapid and complete contaminant degradation can occur with ZVI, but only when direct contact is made between contaminant and the iron surface, and only when contact is made over a significant residence time, as in “funnel and gate”-type barriers where contaminants are forced to cross a ZVI filled trench of adequate thickness;
3. Injecting micro-scale ZVI has not been shown to be commercially viable due to the high cost of fracturing the material into the subsurface and the inadequate distribution of material - not allowing for direct contact to occur;
4. Claims made by manufacturers of vegetable matter/ZVI blends of rapid parent compound degradation without generating daughter products are unfounded and viewed by most in the environmental industry as lacking technical credibility;
5. No credible case studies of vegetable matter/ZVI blends injected into the subsurface to treat a chlorinated ethene plumes have proven to meet the manufacturers’ claims of degrading the parent compound without significant daughter product buildup.

References

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