

FIELD IMPLEMENTATION OF ANAEROBIC DECHLORINATION UTILIZING ZERO-VALENT IRON WITH AN ORGANIC HYDROGEN DONOR

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ABSTRACT: Generally zero-valent iron and anaerobic stimulation utilizing organic hydrogen donors are viewed as stand-alone remedial techniques. The project site, a former research facility which maintained a RCRA storage facility, entailed the application of these two synergistic technologies. As a consequence of the historical use of the area, groundwater and soils had been impacted by chlorinated ethenes and chlorinated ethanes. The integration of the technologies incorporated the delivery of vitamins B₂ and B₁₂, an inorganic oxygen scavenger, an inorganic nutrient addition, an organic hydrogen donor and a 1-3 micron sized zero-valent iron colloidal suspension. Introduction of the materials to the subsurface was accomplished via an innovative direct-push/injection approach, which utilized nitrogen gas, pressure vessels and traditional air diaphragm pumps. Field and laboratory results six months following the injection event including field data loggers for first two months indicate nearly immediate removal of dissolved oxygen and negative oxygen reduction potential of nearly -400 mV. Laboratory data for target compounds, daughter compounds and inorganic compounds demonstrate the efficacy of the remedial program. A complete evaluation of the individual components and the chemistry in-situ at the site indicates that the inclusion of the vitamins and the zero valent iron have provided for dechlorination at high sulfate levels without a c-DCE stall-out and without a lag phase while providing pH control.

INTRODUCTION

Through the years, chlorinated solvents have had a large impact on several industries, including pharmaceuticals, chemical processing, food extraction, dry cleaning, and metal cleaning. With wide spread use and improper handling and storage, extensive soil and water damage has occurred. Due to their toxicity, carcinogenicity, and persistence in the environment, chlorinated solvents are listed by the United States Environmental Protection Agency as high priority pollutants. If left untreated, chlorinated solvents could remain unchanged for a period of fifty years or more. The most common chlorinated solvents used are Methylene Chloride, tetrachloroethene, trichloroethene, carbon tetrachloride, chloroform, tetrachloroethane, dichloroethene and vinyl chloride. Carbon tetrachloride is a systematic poison of the nervous system, the intestinal tract, the liver, and the kidneys. Vinyl chloride and Methylene chloride are known carcinogens, and could also affect the nervous system, the respiratory system, the liver, the blood, and the lymph system.

Chlorinated solvents are often found in separate phases mixtures commonly referred to as dense nonaqueous-phase liquids ("DNAPLs"). DNAPLs are visible, denser-than-water, separate oily phase materials in the subsurface whose migration is governed by gravity, buoyancy, and capillary forces. Chlorinated solvents partition into the water phase to create a dissolved contaminant plume when in contact with water, thus creating a long-term, continuing source of contamination as the soluble constituents slowly dissolve into moving groundwater.

In the second week of June 2003, a series of field injections of remedial liquids, suspensions and gases occurred in the area of a former RCRA storage facility in New Jersey. The objective of the program was to address dissolved and sorbed phase chloroethenes and chloroethanes. The premise of the program was that accelerated dechlorination of soil and water contaminated with chlorinated solvents could be accomplished by stimulating anaerobic microorganisms and thus increasing the rate of biological mineralization of the solvents. This was accomplished by a treatment process consisting of the injection of a colloidal suspension of iron powder (ZVI) with the Hydrogen Release Compound (HRC, a slow release organic hydrogen donor, primarily consisting of a polylactate ester), chemical oxygen scavengers (reducing agents) in solution with essential nutrients (ortho-phosphate and nitrogen compounds), vitamin stimulants B2 and B12 delivered via the compressed gas N₂, so as not to oxygenate an environment targeted for anaerobic processes. The treatment stimulated naturally occurring microorganisms while oxidizing dissolved phase target compounds via the surface action of the iron particles resulting in the breakdown of chlorinated target substrates and their daughter products. It was found that the incorporation of the B₁₂ acts as both an enzymatic stimulus for the anaerobic action and a surface catalyst of the iron particle. It is hypothesized that the core element of the B₁₂, cobalt, enhances the surface oxidation action of the iron.

A closed delivery system was used, utilizing a combination of gas and liquid delivery systems. All of the vessels are interconnected and valved, allowing for mixings, washings, filling, and discharge of materials via pressure vessels or mechanical pumping systems. The system utilized allows for a variety of dissimilar compounds to be delivered via a single injection line. Further, the switching between feed systems is accomplished without any loss of pressure to the delivery line eliminating the common problems experienced from the vacuum developed down-hole as pressure is released and reapplied.

RESULTS AND DISCUSSION

Prior to evaluating the field results an understanding of the daughter product characteristics and how those characteristics relate to those of the mother product was necessary. In particular some method of accounting for the absorbed mass of target compounds on the soils was necessary so that field-sampling data could be better interpreted. Sorption can be defined as the interaction of a contaminant with a solid. More specifically, the term can be further divided into adsorption and absorption. The former refers to an excess contamination concentration at the surface of a solid while the latter implies a more or less uniform penetration of the solid by the contaminant.

Unfortunately, in this environment and most environmental settings, there is no information concerning the specific nature of the interaction. As a result sorption shall be used in a generic way to address both phenomena. As a general rule, assuming a chlorinated solvent is equally distributed between phases is ill advised. As hydrophobic compounds, these solvents will partition preferentially to the soils. Within a system where the pore water occupies 30% of the aquifer volume, two (2) liters of aquifer would contain 600 mls of water and 3500 grams of soil (soil is about 2.5 times more dense than water). As a result, if there was equal distribution of the contaminant between the phases, slightly less than 15% of the contaminant mass would reside within the aqueous phase. Give the hydrophobic nature of the targeted chlorinated solvents much less of the targeted contaminant's mass is found in the dissolved phase. This partitioning is strongly associated with an individual compound's solubility, as the solubility of a hydrophobic compound decreases, the absorption coefficient increases.

When evaluating the adsorption characteristics of individual compounds the Freundlich equation, an empirical equation that is very useful because it accurately describes adsorption data can be applied. This equation is:

$$q_e = KC_e^{1/n}$$

q_e = Surface equilibrium concentration
 C_e = Solution equilibrium concentration
 $1/n$ = unitless constant
 K = Constant

Using published values for Freundlich Parameters:

	K(mg/g)(L/mg)^{1/n}	1/n
Tetrachloroethene	143	0.516
Trichloroethene	56	0.482
<i>t</i> -Dichloroethene	14	0.452
<i>c</i> -Dichloroethene	12	0.587

Thus the individual constants for the mother and daughter compounds may accurately predict dissolved and sorbed phase changes. By assigning a correction factor for the differences in the site's soils and carbon absorption, a calculated dissolved phase for daughter products of the dechlorination process was calculated.

It is the decrease in hydrophobic characteristics of the compounds with each chlorine lost that is responsible for the dramatic decrease in the constant " K ". Thus, as a mole of tetrachloroethene undergoes a single step dechlorination the resulting trichloroethene is nearly 66% less likely to partition to the soil phase at equilibrium. Under these conditions, although there was a *c*-DCE accumulation in the dissolved phase during the first three months, there was no "stall". Therefore, the appearance and disappearance of daughter products was closely related to the sorbed fractions, which in turn was directly related to the soil type in an area and the time that soil has been in contact with varied concentrations of impacted groundwater. As an example, those wells immediately in the source area or down gradient will show higher concentrations of daughter products as a remediation occurs due to the desorption and degradation of the mother product(s) which are more hydrophobic than the daughter products.

Frequently remedial sites show insignificant or incomplete dechlorination, especially those with high aquifer sulfate levels. This potential was particularly a concern at the New Jersey site. It is frequently held that competition of sulfate with the chlorinated organics as an electron acceptor is responsible for this condition. It is generally overlooked that the rapid conversion of sulfate to toxic free sulfide during bacterial reductive dechlorination plays a significant role in the "stalling" of the biotic process. Accumulation of free sulfide is especially important in sites that display both high sulfate and low available iron. Reductive dechlorination inhibition by free sulfide has been observed in microcosms conducted for high sulfate field sites. Free sulfide toxicity to microorganisms can be prevented if ferrous iron precipitates the free sulfide. Further, iron sulfide mineral precipitates have been shown to catalyze reductive dechlorination of chlorinated solvents at rates comparable to metallic iron, on a surface area normalized basis. Microcosms performed at high sulfate sites have been shown to both remove free sulfide toxicity to dehalogenating bacteria and to enhance catalytic reductive dechlorination when ferrous iron is added. Further, ferrous iron, itself, may act as an electron donor. The accumulation and then the disappearance of the ferrous iron species therefore were important in the evaluation of the efficacy of the ability of the program to

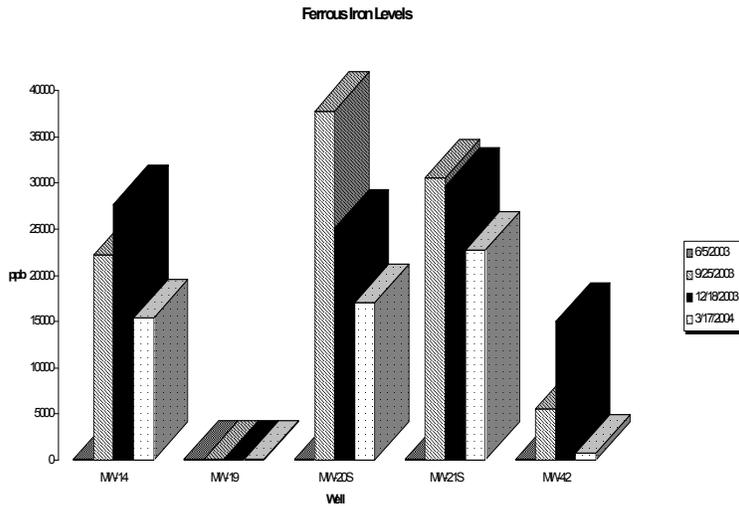


FIGURE 1: Ferrous Iron Across Site

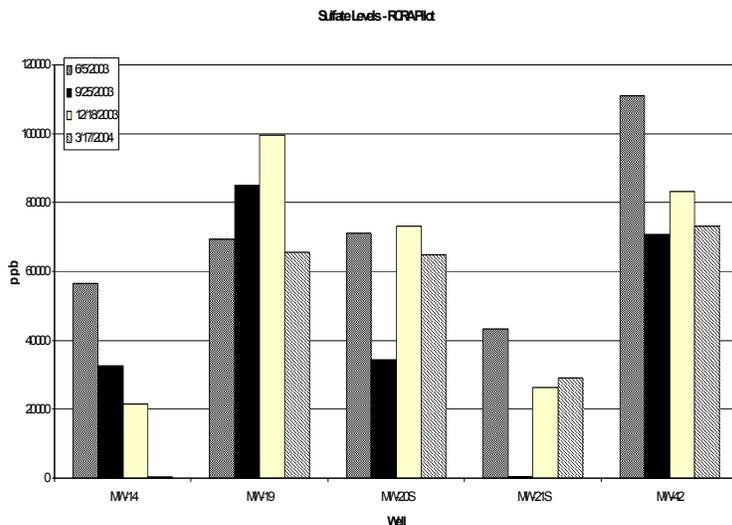


FIGURE 2: Sulfate levels across the treatment area

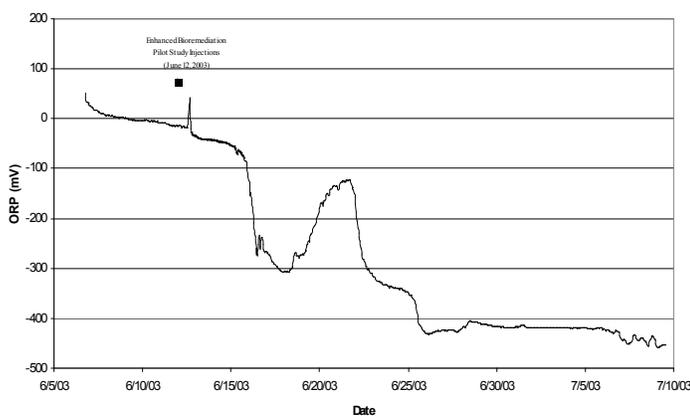


FIGURE 3: Typical Well ORP response following injection event

inhibit the c-DCE stall-out phenomenon (**FIGURE 1**). The effect of the ferrous iron is further confirmed by the sulfate levels observed across the area (**FIGURE 2**).

In any anaerobic reductive dechlorination processes, the efficacy is closely linked to the ability of the chemistry to rapidly achieve and maintain the reductive conditions. Field monitoring of the area through in-situ data loggers allowed for real-time evaluation of this critical component. In all wells the rapid and sustained reductive conditions facilitated anaerobic deductive dechlorination with no apparent lag phase. The down gradient well, MW-14, approximately 20 feet outside of the treatment area, is characteristic of the field ORP data gathered (**Figure 3**). The observed pH, ORP and dissolved oxygen control of the site (**Figure3 and 4**), in conjunction with the ferrous iron data (**Figure 1**), further confirmed the chemistry of program's the ability of the individual components to work together synergistically over time. The data also indicates that the early months of 2004, pH began to decrease due to excessive chloride production. Both the slow releasing polylactate ester and the ZVI have shown to effectively change groundwater conditions to enhance reductive dechlorination of the target

compounds via abiotic and biotic pathways as show below. The most removal has occurred at the down gradient well (MW-20S; **Figure5**) and the cross-gradient well (MW-21S; **Figure 6**), indicating that the plume is effectively contracting as a result of the remedial program.

Further, the generation of daughter products, ethane and ethene indicates that the coordinated abiotic/biotic approach is allowing for a synergistic interaction of the technologies. The rapid production of the gases during the first three months may most probably be attributed to the effect of the iron as well as the anaerobic processes.

Cross-gradient well, MW-21S, experienced in excess of 90% reduction in TCA, 73% reduction in PCE and 60% reduction in the TCE. Initial increases in daughter products in the September sampling event were followed by decreases in the

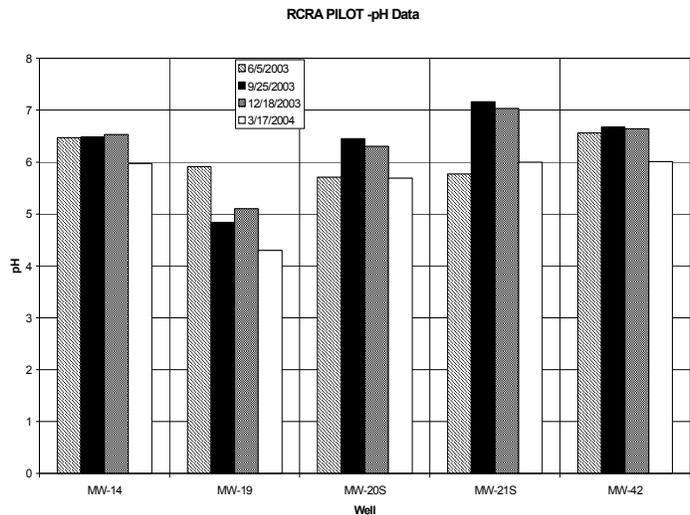


FIGURE 4: Individual Well pH trends through 3/2004

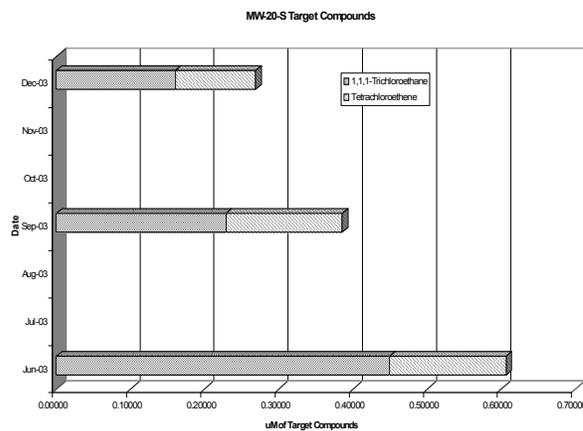


FIGURE 5: Cross gradient monitoring well target compound concentrations

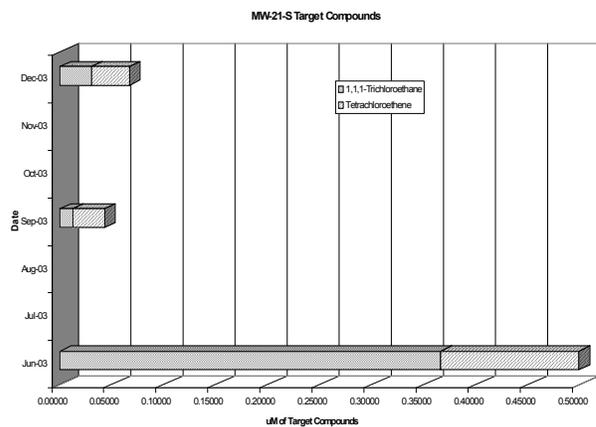


FIGURE 6: Immediately down gradient monitoring well, within treatment targeted compound concentrations

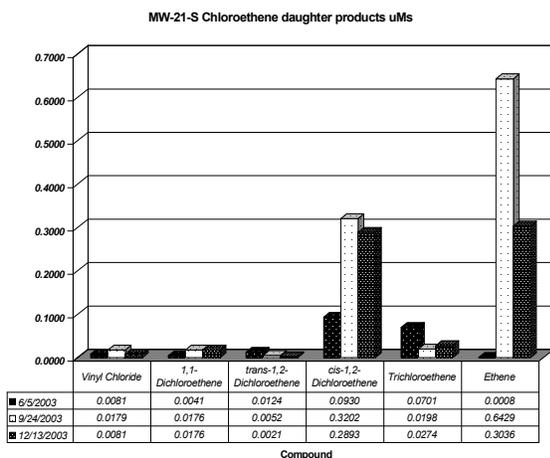


FIGURE 7: Cross gradient chloroethene intermediates

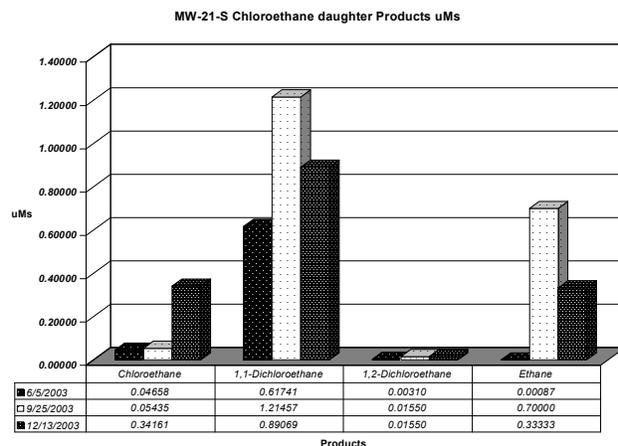


FIGURE 8: Cross gradient chloroethene intermediates

December event, due most probably to the absence of any incursion from the plume (FIGURE 7 & 8).

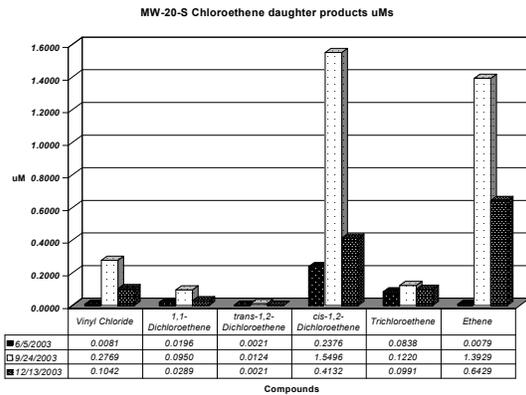


FIGURE 9: Down gradient chloroethene intermediates

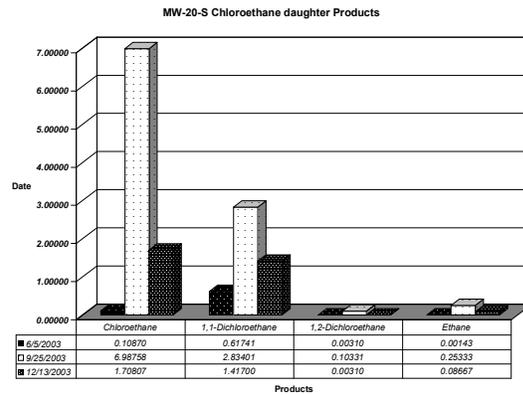


FIGURE 10: Down gradient chloroethene intermediates

Monitoring well 20S saw a decrease in TCA of 65% and a PCE reduction of 30% with a slight increase in TCE of 18%, due primarily to anaerobic activity acting on the PCE. The continued dechlorination of the daughter products seen, in particular the c-DCE indicates a continued mineralization of the sorbed and aqueous target compounds (FIGURE 9 & 10).

CONCLUSION

For the six month period for which data is available, the application of a synergistic application of chemistries which allowed for control of many of the issues facing practitioners of anaerobic processes; rapidly generating reductive conditions, demonstrating dechlorination through to ethane and ethane, minimization of the effects of sulfate, interpretation of c-DCE generation and rapid removal of dissolved phase target compounds.

The utilization of vitamins allows for a reduction in the activation energy required for complete electron transfer through vinyl chloride. By integrating a variety of stimulation and remedial chemistries and applying them via rapid, non-oxygenating processes, the sum action of the individual components is greater than if they were to be used separately. The Vitamin B₁₂ lowers the activation energy required for the electron transfer of the terminal electron to c-DCE, while the core element of the B₁₂, cobalt, catalyzes the surface action of the ZVI. Without the B₁₂, sulfate acts as competitively as a terminal electron acceptor. Vitamin B₂ allows for a more efficient utilization of the hydrogen in the anaerobe, increasing the overall kinetics.

The production of ferrous iron as a consequence of the corrosion of the zero valent iron allows for pH control in a reaction that produces free chloride ions, and thus pH depression. Further, the ferrous and ferric species reduce the free sulfates and sulfides in the environment, allowing for thorough dechlorination without the accumulation of toxic compounds.

The inclusion of the oxygen scavenger, sodium sulfite, produced nearly immediate reducing conditions allowing for maximum utilization of the HRC product as a hydrogen donor rather than an aerobic growth substrate. Thus allowing for more successful use of the organic hydrogen donor, targeting anaerobic processes.

The varied affinities of chlorinated compounds for adsorption to soil is directly tied to the number of chlorine atoms in the molecule. By recognizing that the appearance of c-

DCE is frequently the result of dechlorination of sorbed trichloroethene and tetrachloroethene, rather than the result of a “stall-out” of the anaerobic processes, the field application and understanding of biological processes is more clearly presented. In this way the stoichiometric imbalances seen in mother product disappearance and daughter compound appearance may be resolved.

The valuation of the efficacy of a process or processes, as in the case of synergistic technologies, requires that the entire data set be evaluated with an understanding of the interactions between the inorganic components, field conditions and the degradation pathways of the targeted compounds.