REGENESIS®

Technical Memo

Chlorinated Methane Treatability Study Using Sulfidated Iron and Solid Phase Organic Bioamendments

Introduction

S-MicroZVI® (sulfidated micro zero-valent iron) is an *in situ* remediation product engineered to eliminate toxic soil and groundwater contaminants by chemical reduction. Target contaminants include chloromethanes (e.g., carbon tetrachloride, CT), chlorinated ethenes (e.g., perchloroethylene, PCE, trichloroethylene, TCE) chloroalkanes (e.g., 1,1,1-trichloroethane, 1,1,1-TCA), select pesticides and herbicides, and inorganics such as chromium and arsenic. A key feature of S-MicroZVI is its core shell configuration with an interior consisting of zero valent iron and a surface layer consisting of reduced iron sulfide (mackinawite). The benefits of adding sulfur to zero valent iron have been recognized for almost thirty years[1] with more recent studies showing that sulfidation increases reaction kinetics by over an order of magnitude for relevant groundwater contaminants including TCE.[2-4] Sulfidation also inhibits the unproductive reaction between iron and water that consumes the reactant and lessens its reactive lifetime.[3]

AquiFIX™
Long-Lasting Colloidal Electron Donor

AquiFix has been formulated to be compatible with complimentary remediation amendments such as: S-MicroZVI and PlumeStop® (colloidal activated carbon) without interfering with performance or adsorption.

The benefits of combining zero valent iron and a fermentable organic electron donor to promote faster and more complete remediation are well established.[5] Studies combining sulfidated iron and water-soluble fermentable organics (such as sodium lactate) show rapid TCE degradation kinetics with reduced concentrations of transient daughter products.[5] However, soluble amendments have limited persistence and, in most situations, will be exhausted before S-MicroZVI. Using a long acting, solid phase fermentable organic electron donor can complement the reactivity and persistence provided by S-MicroZVI. AquiFix™ contains small (< 0.5 µm) solid phase organic particles that provide a long-term supply of molecular hydrogen via fermentation by native aquifer microbes to help and sustain bioremediation. Supplemented with a smaller amount of sodium lactate and nutrients, AquiFix provides a unique combination of extended reactivity and subsurface mobility. AquiFix has been formulated to be compatible with complimentary remediation amendments such as: S-MicroZVI and PlumeStop® (colloidal activated carbon) without interfering with performance or adsorption. The performance of AquiFix and PlumeStop for the remediation of chlorinated ethenes has been previously documented in lab and field settings.[6,7]

A treatability study was performed to evaluate the ability of S-MicroZVI and AquiFix to degrade CT and its daughter products, chloroform (CF) and dichloromethane (DCM). Five sets of bottles were prepared: 1) Sterile and untreated (control), 2) A low dose of S-MicroZVI alone (1 g/L solid ZVI basis), 3) A standard dose of S-MicroZVI alone (4 g/L solid ZVI basis), 4) AquiFix alone (10 g/L solid donor basis), and 5) A combination of S-MicroZVI (1 g/L solid ZVI basis) and AquiFix (10 g/L solid donor basis). All bottles were spiked to 400µM CT and equilibrated on a shaker. Treatment efficiency was evaluated by measuring CT, CF, and DCM at two days and then weekly for 60 days and once more at 90 days.

Experimental

Ten 8 oz. amber bottles were prepared for this batch study for each of the five conditions in duplicate:

1. Sterile and untreated control
2. Low dose S-MicroZVI 1 g/L
3. Standard dose S-MicroZVI 4 g/L
4. AquiFix 10 g/L
5. AquiFix 10 g/L and S-MicroZVI 1 g/L

The microcosm bottles were prepared using the following procedures. Each bottle contained 20 g of #90 mesh sand and 230 g of HEPES buffered (pH = 7) argon-sparged (deoxygenated) water. Each microcosm had an initial CT concentration of about 400 µM (~50 mg/L).

1. The sterile and untreated control bottles also contained 4.6 mL of 1% sodium azide. The control bottles were not buffered.
2. The low dose S-MicroZVI bottles also contained 0.6 g of S-MicroZVI.
3. The standard dose S-MicroZVI bottles also contained 2.4 g of S-MicroZVI.
4. The AquiFix only bottles also contained 9.2 g of AquiFix and nutrients. After equilibrating for 24 hr., an anaerobic consortium of dechlorinators (BDI Plus®) was added to a target of 2 x 10^8 cells/L in the bottles.
5. The AquiFix and S-MicroZVI bottles also contained 9.2 g of AquiFix, 0.6 g of S-MicroZVI, and nutrients. After equilibrating for 24 hr., an anaerobic consortium of dechlorinators (BDI Plus) was added to a target of 2 x 10^8 cells/L in the bottles.

All samples were allowed to equilibrate for 24 hrs. on a shaker and analyzed using GCMS and headspace methods to determine concentrations of CT and its chlorinated daughter products. After sampling, the samples were placed back on the shaker and sampled weekly for 60 days and once again at 90 days.

Results and Discussion

Each plot represents the average concentration of the two duplicate bottles used in the experiment.

Sterile Control

The performance of the sterile control microcosms is provided as a dashed line on each graph. The CT concentration declined slowly and after 55 days, remained steady at approximately 75% of the initial amount. It is believed that this decrease was due to slow volatilization from the bottle. As expected, these bottles contained no remediation amendments and experienced no active degradation producing no daughter products.

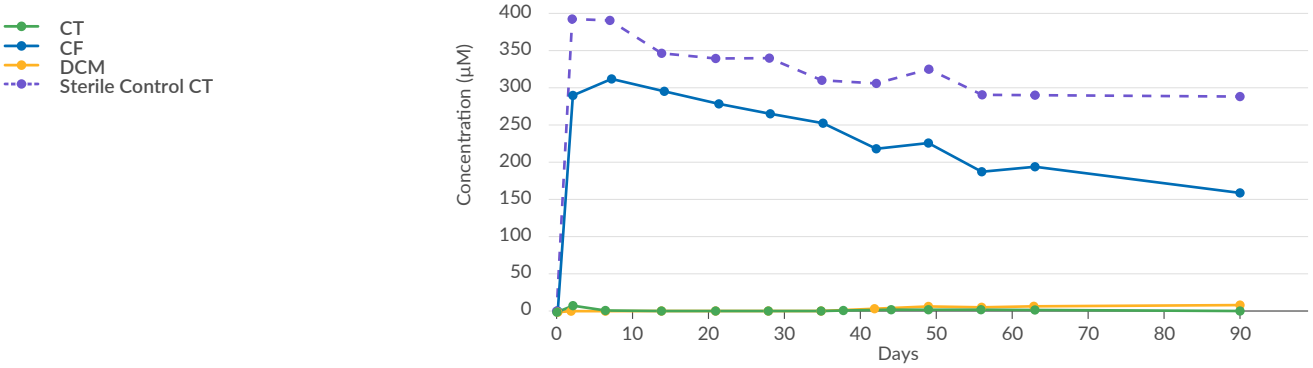
Low Dose S-MicroZVI

The performance of the low dose S-MicroZVI microcosms is provided in Figure 1. S-MicroZVI-alone promoted the rapid and complete removal of CT, with only 3 µM remaining at the first sampling interval (2 days) and non-detect at 7 days. Initially, about 75% of the CT was converted to CF which was partially degraded over the remainder of the experiment. The CF yield is consistent with the reported values of other studies.[8] Chloroform degradation was slower with only minor amounts of DCM produced (4 µM at 90 days). The rapid and complete removal of CT at a low dose demonstrates the ability of S-MicroZVI to rapidly reduce heavily chlorinated compounds while exhibiting slower degradation of partially dechlorinated daughter products.

Figure 1

Low Dose S-MicroZVI (1 g/L)

Contaminant concentrations over time in the 1 g/L S-MicroZVI bottles over 90 days



S-MicroZVI® Sulfidated Zero-Valent Iron

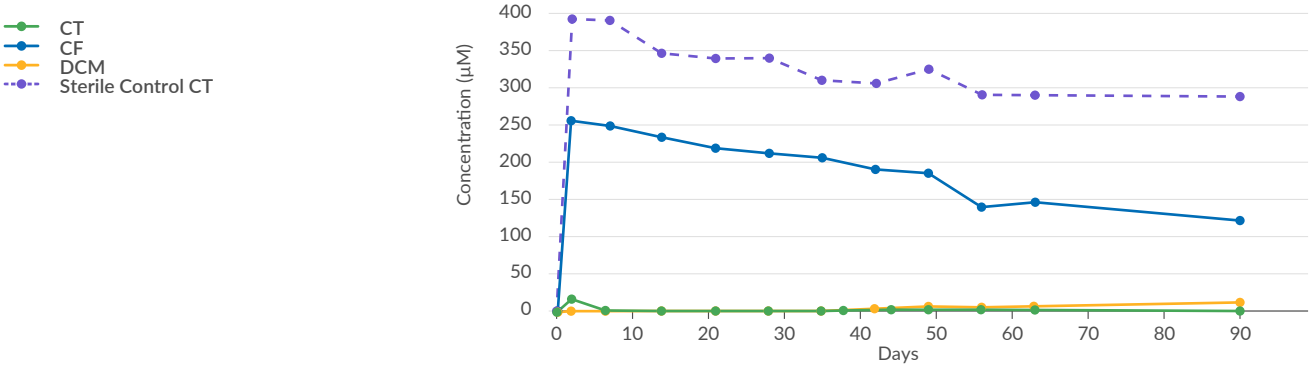
Standard Dose S-MicroZVI

The performance of the standard dose S-MicroZVI microcosms is provided in Figure 2. These behaved similarly to the low dose bottles, with 17 µM CT remaining after 2 days and non-detect after 7 days. Initially, about 65% of the CT was converted to CF which was partially degraded during the remaining 90 days. DCM concentrations at 90 days were minimal (14 µM).

Figure 2

Standard Dose S-MicroZVI (4 g/L)

Contaminant concentrations over time in the 4 g/L S-MicroZVI bottles over 90 days.

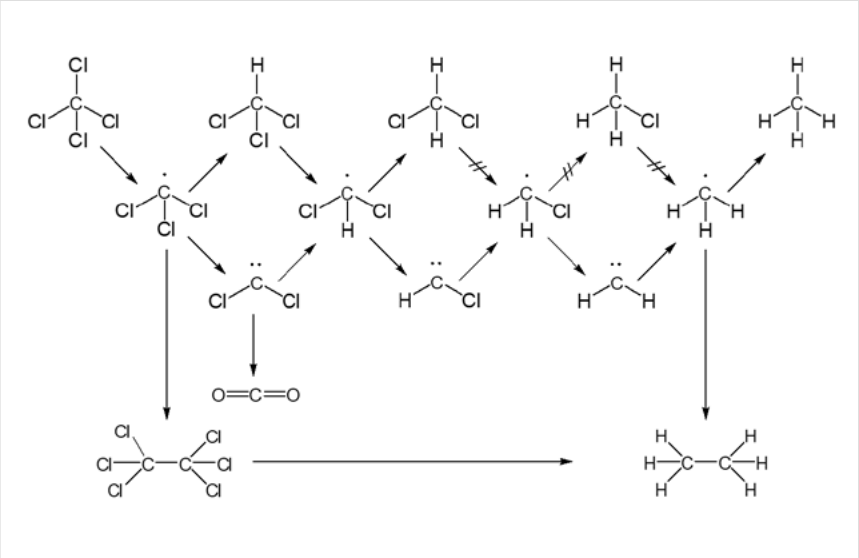


For the ZVI-only microcosms, the non-stoichiometric degradation is consistent with a pathway involving one and two electron free radicals. This pathway produces several terminal degradation products including methane, carbon dioxide, formate, and higher molecular weight hydrocarbons, such as ethane, produced by the coupling of radical species. The degradation pathways are illustrated in Figure 3.

Figure 3

Degradation Pathways

Degradation pathway involving free radicals.



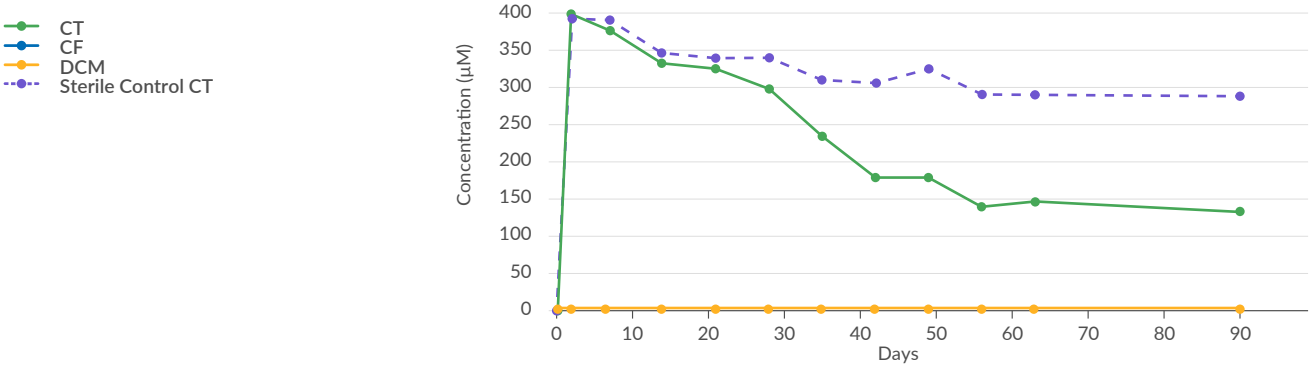
AquiFix Alone

The performance of the AquiFix alone microcosms is provided in Figure 4. During the first 20 days, CT removal was comparable to the sterile control (dashed line) suggesting that minimal degradation had occurred. Subsequently, CT concentrations declined relative to the control and at 90 days the concentration was approximately 40% of the control. Biological degradation through CF and DCM was apparently inhibited by the high concentrations of carbon tetrachloride and the degradation pathway instead possibly included oxidized reaction products such as carbon dioxide or formate.

Figure 4

AquiFix Alone (10 g/L)

Contaminant concentrations over time in the 10 g/L AquiFix bottles over 90 days.



S-Micro ZVI® Sulfidated Zero-Valent Iron

AquiFIX™ Long-Lasting Colloidal Electron Donor

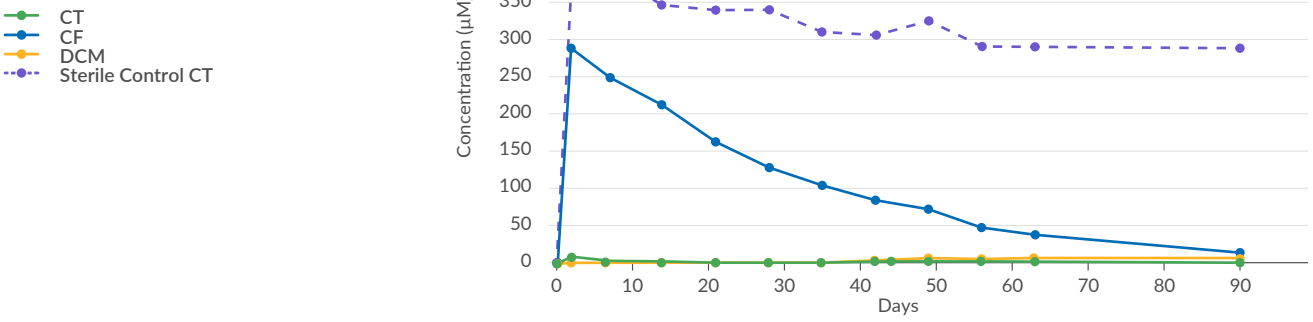
Combined AquiFix and S-MicroZVI

The performance of the combined AquiFix and S-MicroZVI microcosms is provided in Figure 5. The combined system degraded CT to 5 µM after 2 days and to non-detect after 7 days. The initial response is comparable to the S-MicroZVI-only trials, and it is believed that S-MicroZVI-mediated abiotic reactions accomplished almost all the transformation from CT to CF. The CF yield at 2 days was an approximately 62% molar conversion rate, like that observed in the S-MicroZVI only trials. CF degraded steadily throughout the experiment and measured only 12 µM at 90 days with about 6 µM of DCM. After 90 days over 94% of chlorinated methanes were removed from the system compared to the control; this is substantially more than the S-MicroZVI-only microcosms. It is believed that S-MicroZVI-mediated abiotic reactions accomplished most of the CT degradation, and both abiotic and ZVI-accelerated biological processes degraded the chloroform.

Figure 5

AquiFix and S-MicroZVI

Contaminant concentrations over time in the combined 10 g/L AquiFix and 1 g/L S-MicroZVI bottles over 90 days.



Conclusion

A treatability study was performed to evaluate S-MicroZVI and AquiFix performance in degrading carbon tetrachloride (CT) and its daughter products, chloroform (CF) and dichloromethane (DCM). On its own, S-MicroZVI rapidly degraded high concentrations (~ 50 mg/L) of carbon tetrachloride, followed by a slower removal of daughter products. However, when S-MicroZVI was paired with AquiFix, chloroform was eliminated at a considerably higher rate than using SMZVI alone—an important result considering that build-up of chlorinated methanes can have toxic effects on dechlorinating bacteria and prevent biological degradation.

As a result, this study demonstrates that combining abiotic (S-MicroZVI-driven) and biotic (dechlorinating bacteria-driven) treatment approaches is synergistically beneficial for remediating chlorinated methanes and ethenes (such as PCE, TCE, and subsequent daughter products). Additionally, with a 10-year estimated hydrogen release profile, AquiFix will fuel the biotic reduction of these contaminants in the field over the long term, enabling this synergy until S-MicroZVI becomes depleted.

References

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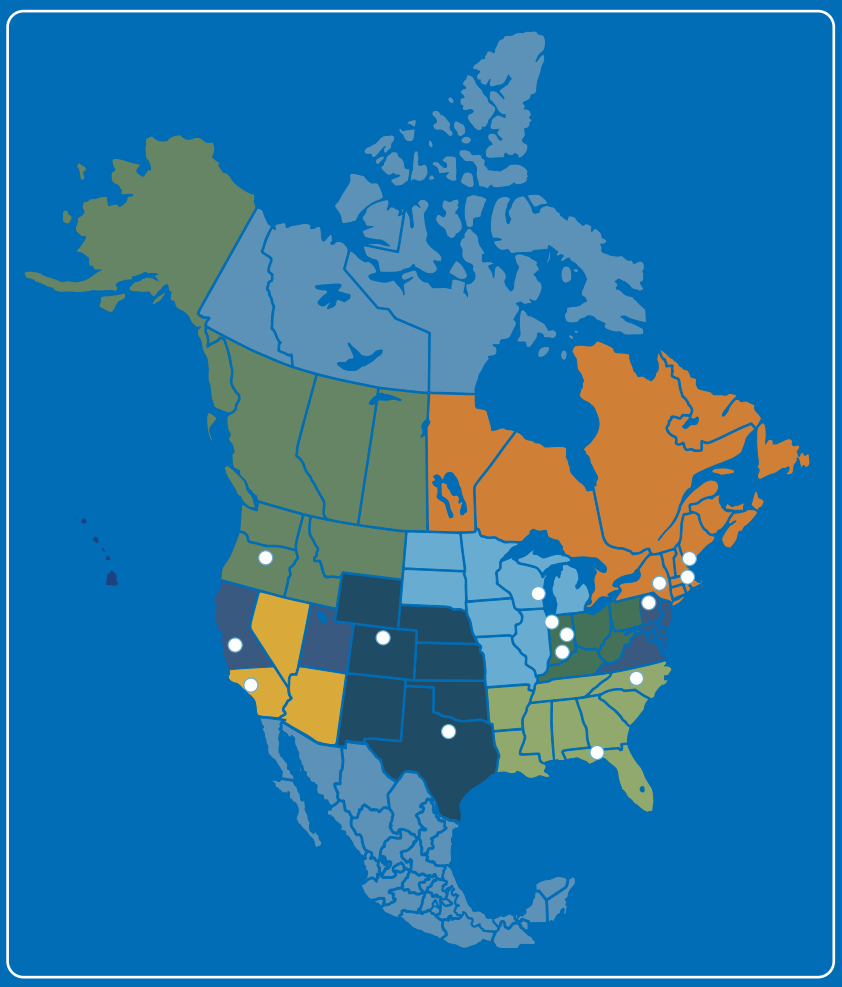

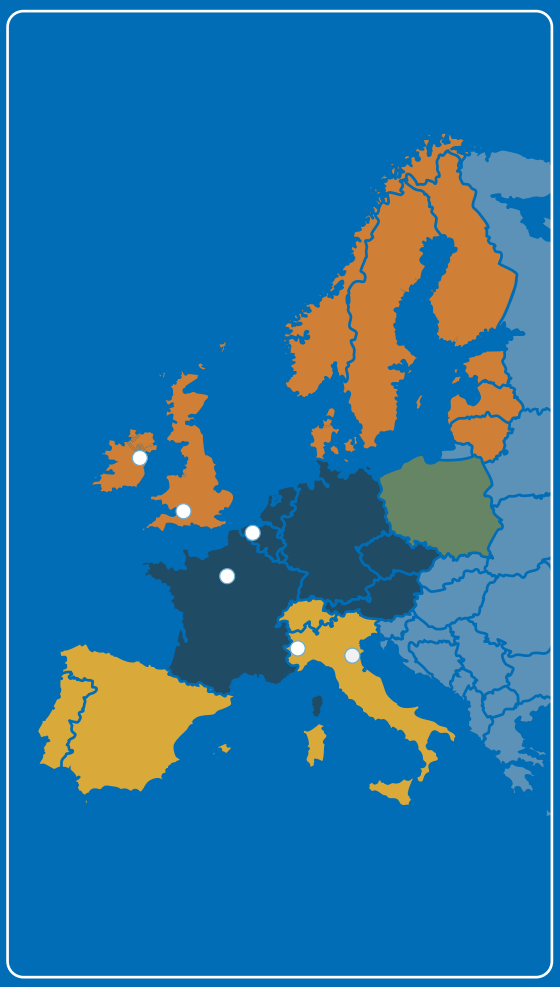

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