Optimization of ZVI Technology for In-Situ Remediation of Chlorinated Hydrocarbons: The Performance of Injectable Water-Based Iron/Iron Sulfide Formulations
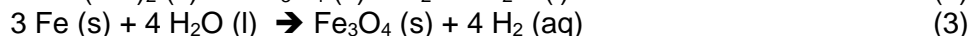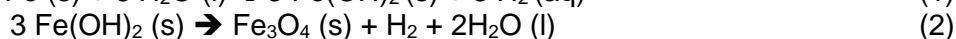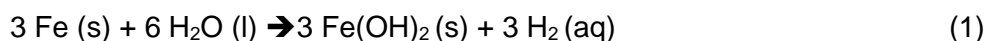
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ABSTRACT: Zero valent iron and reduced iron sulfides can accomplish the rapid and complete abiotic electrochemical reduction of trichloroethylene (TCE) and other chlorinated hydrocarbons. The objective of this study was to investigate the performance of water-based, injectable iron/iron sulfide remediation amendments to facilitate the accelerated abiotic degradation of aqueous phase TCE. Four products were investigated. 1) OnMaterials' AquaMetal ZVI consisting of 2-3 micrometer average particle size iron suspended in water (AMZVI); 2) OnMaterials' AquaMetal ZVI with iron sulfide additions (AMZVI:S); 3) Microscale iron (Peerless 90D grade) and; 4) Carbonyl iron (BASF OM grade). Each material exhibited first order rate kinetics with TCE. Mass normalized rate constants for TCE ranged from a low of 0.0126 L g^{-1} day^{-1} for carbonyl iron to high of 0.337 L g^{-1} day^{-1} for AMZVI:S. Sulfide additions also provided the benefit of lessening the reaction rate of ZVI with water; extending reactive capacity and persistence.

INTRODUCTION

ZVI is a powerful reductant that is capable of eliminating chlorinated ethenes and other toxic groundwater contaminants primarily through beta-elimination reactions which bypass toxic daughter products that are produced by hydrogenolysis reactions (Roberts et al. 1996). Reduced iron (II) sulfide is another reductant capable of eliminating chlorinated ethenes through similar mechanisms (Butler and Hayes. 2001). The benefits of using mixed iron/iron sulfide reductants have been known for over 20 years with somewhat limited commercial use (Sivavec et al. 1996).

Dry zero valent iron powder has an oxide surface layer that forms during powder synthesis and subsequent exposure to air. Similarly, aqueous phase reactions can passivate ZVI surfaces with iron hydroxides, iron oxyhydroxides, and iron oxides; an example of an aqueous phase reaction resulting in passivation is shown in equations (1) – (3). This reaction is consistent with the presence of iron oxyhydroxide (FeOOH) and magnetite surfaces (Fe_3O_4) often found in aqueous phase NZVI products (Liu et al. 2015).

$$3\ Fe\ (s) + 6\ H_2O\ (l) \rightarrow 3\ Fe(OH)_2\ (s) + 3\ H_2\ (aq) \tag{1}$$
$$3\ Fe(OH)_2\ (s) \rightarrow Fe_3O_4\ (s) + H_2 + 2H_2O\ (l) \tag{2}$$
$$3\ Fe\ (s) + 4\ H_2O\ (l) \rightarrow Fe_3O_4\ (s) + 4\ H_2\ (aq) \tag{3}$$

Other aqueous phase reactions occur with common groundwater anions, including the formation of iron carbonate and iron phosphate can also passivate the iron surfaces and further inhibit reaction kinetics. Because of these passivating surface layers, observed reaction kinetics with groundwater contaminants are slower than those provide by reduced zero valent metal alone.

Recently, sulfidized nanocrystalline zero valent iron (s-NZVI) have been the subject of research efforts with a primary focus on maximizing reaction rates with contaminants in relation to wasteful reactions with water (Fan et al. 2016). The methodology used to sulfidize ZVI is straightforward (Hassan. 2000) and can be introduced into the AquaMetal ZVI manufacturing process. These synthesis techniques employ the aqueous phase electrochemical reduction of sulfate, sulfite, hyposulfite, or sulfide compounds with ZVI. As an example, the reaction of ZVI with aqueous phase sulfate is shown in equation (4); similar reactions occur with other sulfur containing compounds.

$$4\ Fe\ (s) + SO_4^{-2}\ (aq) + 4\ H_2O\ (l) \rightarrow FeS\ (s) + 3\ Fe(OH)_2\ (s) + 2\ OH^-\ (aq) \tag{4}$$
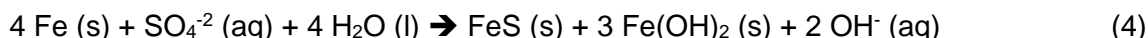
The ability to synthesize iron particles with surfaces containing iron sulfide has the potential to minimize aqueous phase reactions with water, dissolved oxygen and other aqueous phase anions that result in passivating surface layers. Beyond the benefits of minimizing reactivity with water, prior work has shown that mixed iron/iron sulfide products exhibit accelerated reaction kinetics with chlorinated ethenes (Sivacec et al., 1996).

In summary, the ability to accomplish the aqueous phase synthesis of mixed iron/iron sulfide in situ remediation amendments provides an opportunity to accelerate reaction rates with groundwater contaminants, decrease unnecessary reactions with of iron with water, and improve the quality of aqueous phase suspensions for better subsurface distribution.

MATERIALS AND METHODS

Z-Loy^{TM} AquaMetal ZVI is synthesized using a proprietary process where zero valent iron powder is mechanically processed to a particle size of about 2 to 3 micrometers. After synthesizing 40 wt.% ZVI in municipal water, sulfide was added immediately added to the AquaMetal ZVI suspension using a proprietary process. Materials were allowed to age for 30 days before testing reactivity in an attempt to equilibrate aqueous phase reactions with iron.

Treatability studies evaluated reactivity of four compositions. Each composition was tested in replicate using two individual microcosm bottles. Greater doses were used for the dry powders due to slower kinetics and the need to shorten the duration of the treatability study.
  1) Z-Loy^{TM} AquaMetal ZVI with 2 mol% sulfide (AMZVI:S) – 2.0 g/L
  2) Z-Loy^{TM} AquaMetal ZVI without sulfide additions (AMZVI) – 2.0 g/L
  3) Carbonyl iron powder (BASF OM grade) – 10.0 g/L
  4) Microscale iron powder (Peerless 90D) – 10.0 g/L

Microcosm bottles were prepared by using pH 7.1 0.05 M HEPES buffered municipal water. 80 g of buffered water was added to 240 mL screw top amber bottles with Teflon septa and 200 g sand. Zero valent iron amendments were then added and the bottles were flushed with nitrogen gas. After the caps were applied the bottles inverted several times to homogenize the mixture. 2.0 μL of TCE was added through the septa using a microliter syringe for an initial contaminant concentration of about 36 mg/L TCE. The bottles were inverted and set cap side down without agitation in a temperature controlled enclosure at 25C.

Contaminant concentrations were measured at days 1, 3, 5 and 7 by withdrawing 50 μL of headspace gas and injecting this into a Perkin Elmer Clarus GC with an ECD detector; TCE concentrations were measured using integrated peak areas. Degradation kinetics were measured by plotting ln [TCE area counts] vs. time. The ECD detector cannot resolved cis-1,2-dichlorethene (c-1,2-DCE) or vinyl chloride (VC) daughter products at these concentrations although it is anticipated that the accumulation of these daughter products is minor. The first order rate constants (k_{obs}) were taken directly from the slope of the linear regression for a plot of ln [Area Counts] versus time. A mass adjusted rate constant was calculated using equation (5).

$$K_{obs} \text{ (day}^{-1}) = K_{mass} \text{ (L g}^{-1} \text{ day}^{-1}) * \text{ZVI dose (g/L)} \qquad (5)$$

RESULTS AND DISCUSSIONS

TCE Rate Constants. The average rate constant for the average of two microcosm bottles studied for each material is provided in Table 1. The first order kinetic plot for each material had a correlation coefficient (R^2) of greater than 0.996 indicating that first order reaction kinetics were followed and degradation rates changed little over the seven-day experiment period.

TABLE 1. Average rate constants for TCE degradation (25C).

Material ID	Dose (g/L)	K_{obs} (day^{-1})	K_{mass} (L g^{-1} day^{-1})	R^2
AMZVI:S	2.0	0.6740	0.3370	0.996
AMZVI	2.0	0.0599	0.0300	0.999
BASF OM CIP	10.0	0.1257	0.0126	0.998
Peerless 90D	10.0	0.2030	0.0203	0.998

Effect of Sulfide Additions. Figure 1 shows first order kinetic rate plots comparing the kinetics of microcosm bottles with 2.0 g/L AMZVI:S and AMZVI. Both materials exhibited first order rate kinetics with the sulfidized material providing an approximate 11 fold increase in reaction rate. The kinetic enhancement is consistent with previously reported data (Han and Yan. 2016). Beyond increases in kinetics; substantially less gas pressure buildup was noticed in the bottles dosed with AMZVI:S, consistent with slower reaction kinetics with water when using sulfidized iron.

Comparison of AMZVI:S Kinetics with Commodity ZVI Products. Figure 2 shows first order rate kinetic plots comparing the microcosm bottles with 2.0 g AMZVI:S, 10 g/L BASF OM grade carbonyl iron powder, and 10 g/L Peerless 90D microscale iron. Once again, each material exhibited first order reaction kinetics. The mass normalized rate constant for AMZVI:S was about 27 times that of the carbonyl iron and 17 times that of coarser microscale iron. Kinetics for the larger particle size Peerless iron product were about 80% greater than carbonyl iron, corroborating earlier results (Han and Yan. 2016).
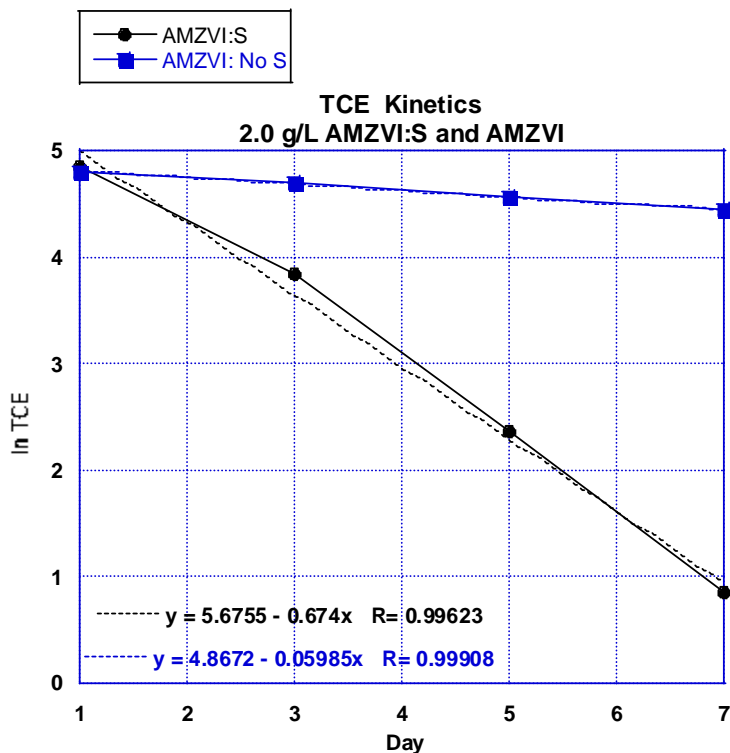

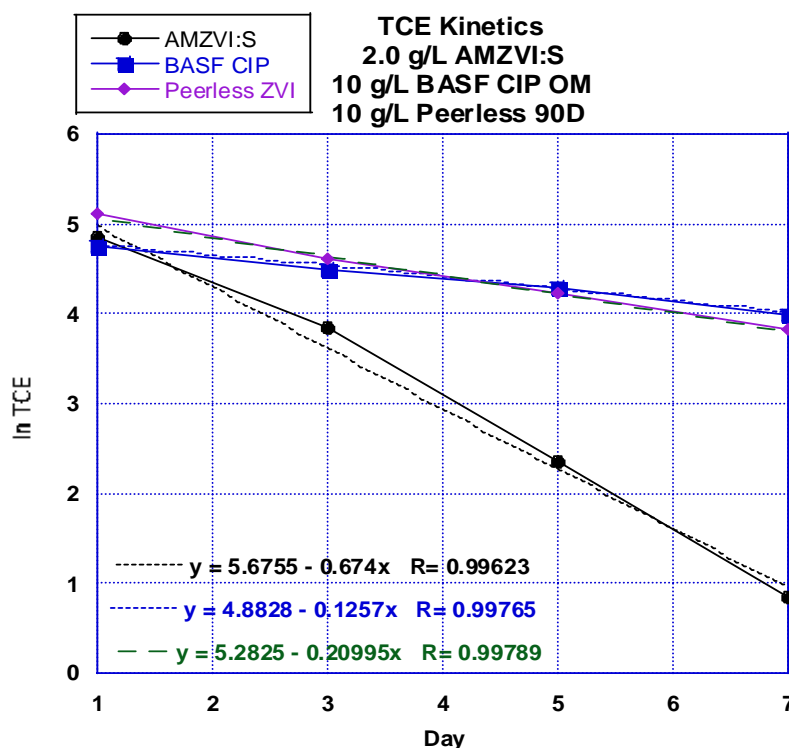**FIGURE 1. First order rate constant for AMZVI:S and AMZVI both 2.0 g/L.**

FIGURE 2. First order rate constant for AMZVI:S and AMZVI both 2.0 g/L.

CONCLUSIONS

Treatability studies demonstrated the ability of mixed iron/iron sulfide amendments to accomplish the rapid elimination of aqueous phase TCE. Small sulfide additions (2 mol%) yielded a more than 10-fold increase in reactivity compared to iron alone. Reactivity was about 20 to 30 times greater than that provided by commercially available dry ZVI products. Beyond reactivity enhancement, the sulfidized material appeared to lessen reactivity with water, potentially extending the material's reactive capacity and persistence.

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