Evaluating Trichloroethylene Degradation Using Differing Nano- and Micro-Scale Iron Particles

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ABSTRACT: Trichloroethylene, or TCE, is a central nervous system depressant and possible carcinogen, as well as a persistent groundwater pollutant. TCE exists in the aquifer either as free product in the form of a dense non-aqueous phase liquid (DNAPL) or as a dissolved-phase constituent. It is only slightly soluble in water, so dissolution of the contaminant is a long-term process and *in-situ* remediation is difficult. To remedy this, NASA and the University of Central Florida developed Emulsified Zero-Valent Iron, or EZVI. The emulsion droplet contains ZVI particles and water encapsulated by an oil/surfactant membrane, and effectively penetrates to degrade DNAPL-phase TCE. To maximize the efficiency of this process, several commercially available ZVIs of radically different particle sizes and morphologies both in emulsion and as neat (unemulsified) metal were evaluated for relative effectiveness at TCE degradation.

INTRODUCTION

TCE was widely used as an industrial solvent and degreaser until the 1970s, and through improper disposal practices, has become ubiquitous in the environment. Remediation of TCE is of great concern because it is both toxic and, persistent in the environment. The persistence of TCE contamination is a result of its low solubility in water, making dissolution a long-term process. Upon entering the environment, the DNAPL-phase TCE permeates through the subsurface soil and sinks into the groundwater until it is contained by a non-permeable surface such as bedrock. At this point, it pools and slowly dissolves into any water that it comes into contact with. Consequently, the pool continually contaminates groundwater over time. Because the groundwater is in constant motion, a single DNAPL pool source can contaminate a tremendous volume of potential drinking water. (Brooks, 2000). Left untreated, the TCE remains in groundwater indefinitely without appreciable degradation. Some bioremediation may occur, however it is sporadic and usually incomplete.

The ability of zero-valent iron (ZVI) to reductively dehalogenate chlorinated solvents down to the parent hydrocarbon skeleton has previously been demonstrated (Quinn et. al., 2005). The ZVI reduces TCE by catalyzing its degradation pathway as a temporary electron donor. Therefore, iron will degrade TCE as long as it is in contact and has a supply of electrons from the metal and proton donation from water. This phenomenon has been exploited in permeable reactive barriers (PRBs) utilizing ZVI as the reactive material. PRBs have been employed in treating plumes of chlorinated solvents in the dissolved phase with some success (O'Hannesin and Gillham, 1998; Vogan *et al.*, 1999). Althoough PRB technology is passive and requires no energy, it still necessitates transport of the dissolved phase chlorinated solvents to the barrier for treatment, and is therefore, unable to treat the DNAPL pool contamination source. To remedy this, Emulsified Zero-Valent Iron (EZVI) was developed by NASA and the University of Central Florida. EZVI is composed of food-grade surfactant, biodegradable oil, water, and ZVI particles (either nano- or microscale iron). The emulsion droplet contains ZVI particles and water encapsulated by an oil/surfactant membrane. Both TCE and the exterior membrane are hydrophobic. Thus, TCE can dissolve into, and diffuse through the membrane into the interior reactive zone of the droplet where it is degraded. This allows the emulsion to effectively penetrate and degrade DNAPL-phase TCE. The emulsion is advantageous because it can be injected deeper into the subsurface than is practical for conventional PRB applications, and can be injected directly into DNAPL source areas for direct treatment (O'Hara, *et. al.*, 2006). Moreover, EZVI promotes bioremediation by providing a carbon source (the oil) for the microbes that naturally degrade TCE. The effectiveness of this EZVI technology for remediation of chlorinated solvents in soil and groundwater has been demonstrated extensively both on the lab bench and in the field.

Although effective, nanoscale zero-valent iron is considerably more expensive than its microscale counterpart. Thus, the cost of materials can be reduced significantly if successful remediation is achievable using emulsions containing iron powders of larger particle size. This project focused on maximizing the efficiency of EZVI by comparing the reactivities of several commercially available micro- and nano-scale brands of zero-valent irons with respect to DNAPL phase TCE degradation in their emulsified and neat metal forms. The findings of this study may help guide selection of the most cost effective zero-valent iron for use in future large-scale remediation efforts.

MATERIALS AND METHODS

Materials. Five iron powders with radically different morphologies and specific surface areas were selected for evaluation. Two of these brands consisted solely of nanoscale size particulate iron: one from Toda Kogyo Corp. of Japan, size range 100-200 nm, and another from OnMaterials Corp., with particles of approximately 250 nm in diameter. To protect the ZVI from oxidation, the former was shipped and stored in a 50% by weight deoxygenated water slurry and the latter under 33% glycol. Another distributor, ASAT Inc., supplied two more brands of iron for evaluation. One of these was a blend of nano- and microscale components, ranging in size from 200 nm-3 μm. The other was comprised of microscale particles ranging from 1-3 μm. The fifth brand, from BASF, consisted of particles with diameters ranging from 1-5 μm. The ASAT and BASF brands were shipped and stored dry. Images of the microscale powders were obtained using scanning electron microscopy (SEM), and quantitative fluorescence confocal laser scanning microscopy (CLSM) was used for the nanoscale slurries.

Methods.

DNAPL Phase TCE Exposure to Emusified ZVI. Emulsions were prepared from each of the five iron powders under an inert nitrogen atmosphere. Each emulsion consisted of 80.0 mL corn oil, 100.0 mL deoxygenated deionized water, 3.0 mL Span 85 (a food grade surfactant), and 20.0 g of the respective iron powder. To the dry powders, 10.0 mL of a 0.01N hydrochloric acid solution was added to remove the oxide layer on the particle surface. This volume was counterbalanced in the subsequent water addition step. The OnMaterials iron was unable to produce a stable emulsion and was dismissed as a candidate for further evaluation.

A series of reaction vials were prepared from each of the remaining four stable emulsions (TODA, BASF, ASAT nano/micro blend, and ASAT miroscale). To each vial 5.0 g of emulsion and 10 mL of deoxygenated deionized water were added. These vials were inoculated with a 100 μL aliquot of neat TCE. Subsequently, the vials were sealed and placed upon a shaker table until analysis.

DNAPL Phase TCE Exposure to Neat ZVI. A series of reaction vials was prepared to compare the DNAPL phase TCE degradation capabilities of each of the four iron powders studied in emulsified form (TODA, BASF, ASAT nano/micro blend, and ASAT miroscale) to those of the iron powders in neat form. These reaction vials were prepared under an inert nitrogen atmosphere. To each vial, 1.0 g of the respective iron powder and 10 mL deoxygenated deionized water was added. Each vial was inoculated with a 100 μL aliquot of neat TCE, sealed, and placed on a shaker table until analysis.

Acid Washing for ZVI Activation. As the aforementioned emulsified iron powder study proceeded, it became apparent that the dry powder irons (BASF, ASAT nano/micro blend, and ASAT miroscale), were not reactive in emulsified form. Unlike the TODA iron, which was shipped and stored in a protective water slurry to prevent oxidation, these iron powders required acid washing prior to emulsification.

To determine if the inactivity of the emulsion was due to inadequate removal of the surface oxide layer on the iron particle surface, two more emulsions were prepared from the BASF and ASAT nano/micro blend iron powders respectively. This time, a stronger hydrochloric acid solution (0.10 N HCl) was used to acid wash the iron particles. The emulsions were prepared immediately after acid washing, and the formulation of oil, water, iron, and Span 85 was unchanged. A series of reaction vials were prepared from the two emulsions. To each vial 5.0 g of emulsion and 10 mL of deoxygenated deionized water were added. These vials were inoculated with a 100 μL aliquot of neat TCE. Subsequently, the vials were sealed and placed upon a shaker table until analysis.

Headspace Analysis. Ethene, ethane, and acetylene are the 2-carbon containing (C_2H_x), nonhalogenated by-products of TCE degradation. Therefore, the presence of these C_2H_x gases was used to quantify the degradation of TCE over time.Vial headspace samples were extracted periodically and analyzed using an HP5890 gas chromatograph equipped with a flame ionization detector (GC/FID) over a reaction time of several weeks. The headspace of the experimental vials was intoduced for analysis via the evacuated ports of a Tekmar autosampler connected to a purge and trap concentrator.

RESULTS AND DISCUSSION

Analytical results revealed that the reaction vials containing the BASF iron powder in both the neat and emulsified forms were compromised. This may have been due to surface stabilization methods utilized by the manufacturer. Further investigation is currently underway to determine the cause of the failure of these particles to react with the DNAPL phase TCE. Additionally, performance assessment of the OnMaterials iron was abandoned because a stable emulsion could not be produced from this material. This was likely a result of the protective glycol coating in which this material was shipped interfering with the emulsion formulation. Thus, the data from three of the five brands of iron originally selected for evaluation are presented here.

Imaging of Iron Particles. The SEM micrographs of the different iron particles exposed dramatic morphological and structural differences differences as presented in Figures 1-3.

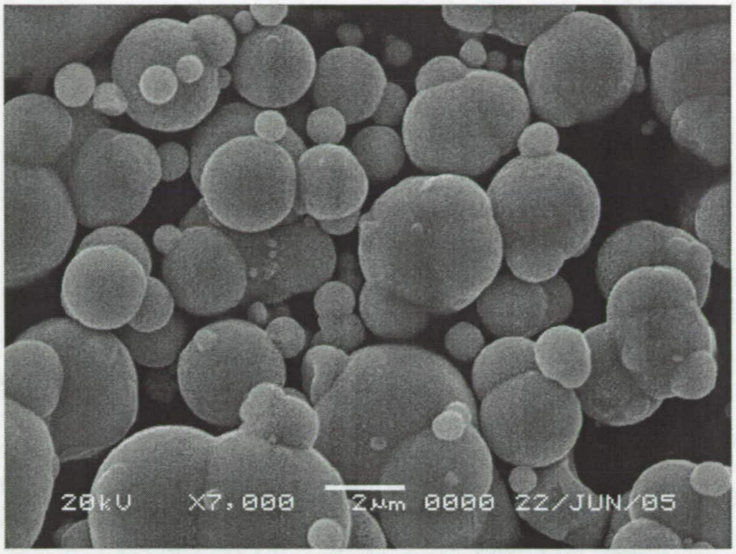

FIGURE 1. BASF iron particles (7000x)

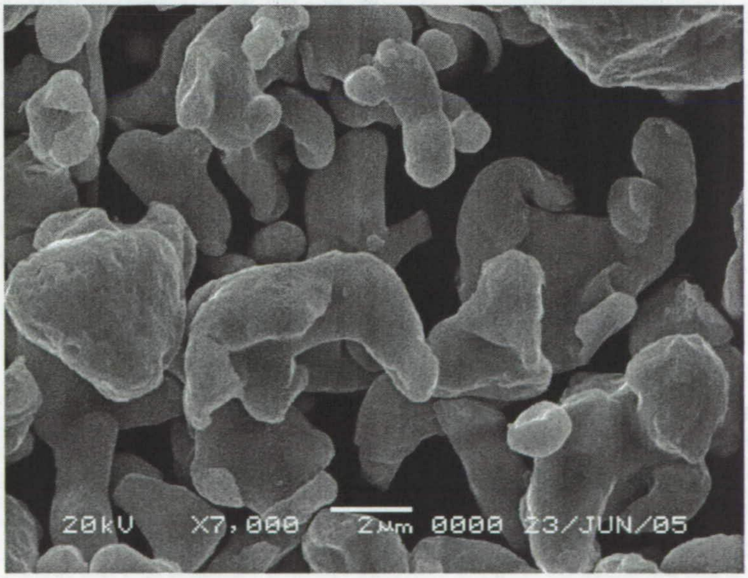

FIGURE 2. ASAT microscale iron particles (7000x)

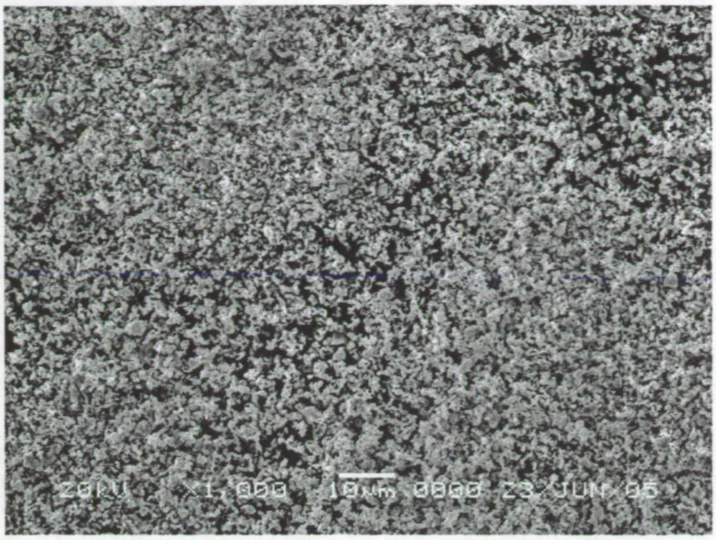

FIGURE 3. ASAT nano/micro blend (1000x)

DNAPL Phase TCE Exposure to Neat ZVI.
The TODA, ASAT nano/micro blend, and ASAT microscale iron particles demonstrated the ability to reductively dehalogenate DNAPL phase TCE in neat form by production of the C_2H_x degradation by-products. Production of C_2H_x by the ASAT microscale iron particles occurred at a slower initial rate. However, after a reaction time of 21 days, the quantity of C_2H_x produced by the microscale particles is comparable to that produced by the nanoscale particles.

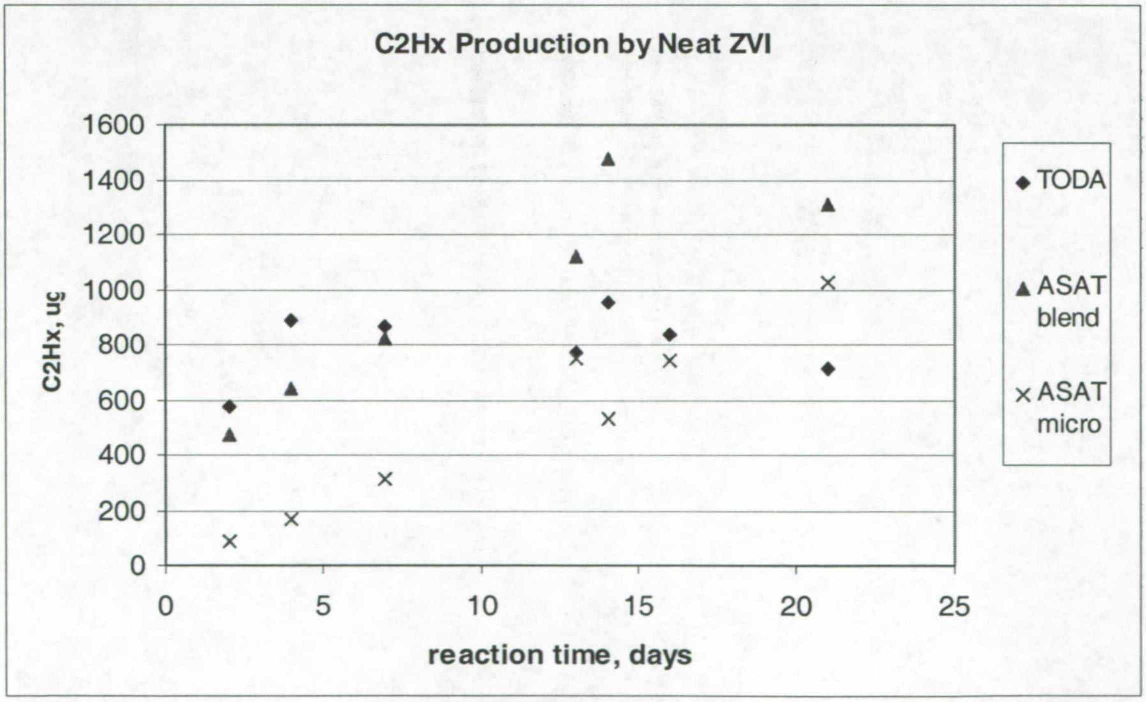

FIGURE 4. Production of TCE degradation by-products over time different iron particles in neat form

DNAPL Phase TCE Exposure to Emusified ZVI. Headspace analysis of the initial four emulsions prepared for this study showed that only the emulsified TODA iron particles exhibited the capability to degrade DNAPL phase TCE.

Acid Washing for ZVI Activation. The stronger (0.10 N HCl) acid wash solution successfully activated the reactive surface of the ASAT nano/micro blend iron particles as demonstrated by the ability of these particles to degrade DNAPL phase TCE in emulsified form. The performance of this activated emulsion in comparison to the initial TODA emulsion is presented in Figure 6. Also presented, is the performance of the initial ASAT nano/micro blend emulsion containing the iron particles that did not respond to the weaker acid surface treatment.

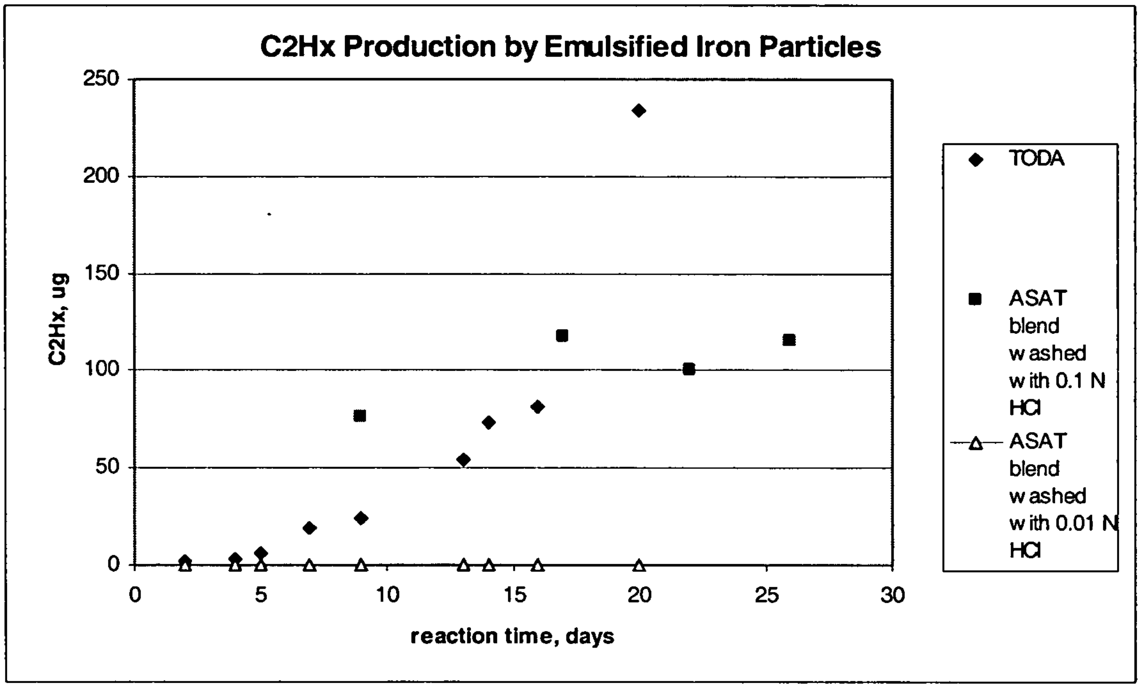

FIGURE 5. Production of TCE degradation by-products over time by several by different emulsified iron particles

CONCLUSIONS

The ASAT microscale iron particles in neat form exhibited capabilities for TCE degradation similar to those of the TODA nanoscale or ASAT nano/micro blend. However, the initial degradation rate is slower for the larger particles.
Also, the importance of using an appropriate acid wash solution to remove the oxide layer on the reactive surface of the iron particle was observed. The emulsified ASAT nano/micro blend responded positively to surface treatment with a stronger acid wash. Although not tested, it is reasonable to assume that the ASAT microscale material would respond in kind.