

The In Situ Treatment of DNAPL with Zero-Valent Iron Emulsions

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This study demonstrated the feasibility of using emulsified nanoscale and microscale iron particles to enhance dehalogenation of dense non-aqueous phase liquid (DNAPL) free-phase. The emulsified system consists of a surfactant-stabilized, biodegradable oil-in-water emulsion with nanoscale or microscale iron particles contained within the emulsion micelles. It was demonstrated that DNAPLs, such as TCE, diffuse through the oil membrane of the emulsion micelle whereupon they reach the surface of an iron particle and dehalogenation takes place. The hydrocarbon reaction by-products of the dehalogenation reaction, primarily ethene (no chlorinated products detected), diffuse out of the emulsion micelle. This study also demonstrated that an iron-emulsion system could be delivered in-situ to a DNAPL pool in a soil matrix by using a simulated push well technique. Iron emulsions degraded free-phase TCE at a rate comparable to the degradation of dissolved-phase TCE by iron particles, while pure iron had a very low degradation rate for free-phase TCE. The iron-emulsion micelles can be injected into a sand matrix where they become immobilized

Remediation of chlorinated solvents in ground water is most commonly attempted by using pump and treat technology. It is now widely recognized that due to the slow dissolution of solvents from residual or pooled DNAPL sources, pump and treat primarily provides containment, rather than remediation. Because of this slow dissolution, pump and treat systems operate for long periods of time (i.e. decades) in order to maintain protection of human health and the environment, incurring high operation and maintenance costs. . There is a critical need for technologies that can effectively treat DNAPL sources in the saturated zone with reduced treatment times and lower costs.

The emulsified system consists of a surfactant-stabilized, oil-in-water emulsion with the nanoscale iron particles contained within the emulsion particles. DNAPLs, such as TCE, diffuse through the oil membrane of the emulsion micelle whereupon they reach the surface of an iron particle where dehalogenation takes place. The hydrocarbon reaction by-products of the dehalogenation reaction diffuse out of the emulsion particle and vent to the ground surface. The iron-emulsion system can be delivered in-situ to the DNAPL pool through a series of push wells.

With iron-emulsion systems, it is desirable to use the smallest iron particles possible. Smaller sized particles produce a more stable and reactive emulsion that is capable of penetrating even the narrowest pores between soil particles. Thus, it is desirable to use iron particles in the nano or microscale size range. The nanoscale iron has a surface area between 15 and 25 m²/g and has

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been demonstrated to be active in the dehalogenation of TCE in groundwater (Wang and Zhang, 1997; Ruiz, 1998). Nanoscale iron can be mixed directly with water to form an iron slurry that can be injected into the ground to intercept or treat a plume of contaminated groundwater. However, if this aqueous slurry is to be used to treat a DNAPL pool, the hydrophobic contaminant would reject the hydrophilic slurry and the iron particles would not be delivered to the DNAPL-phase TCE. Thus, it is necessary to make the iron particle slurry hydrophobic.

There is a large scientific basis for the production of what is known as liquid membranes (Cahn et al., 1974; Kim et al., 1983). These liquid membranes are emulsion particles that can be made to have a spherical, hydrophobic skin and an aqueous hydrophilic interior. The iron particles are contained in the aqueous interior sphere. The exterior of the particle is hydrophobic and is capable of penetrating a separate DNAPL phase. The chlorinated solvent dissolves into the hydrophobic emulsion membrane and moves by diffusion into the aqueous interior. The dehalogenation reaction rapidly takes place at the surface of the iron. A graphic rendition of the emulsion system at the microscopic level is shown in Figure 1. The liquid membrane emulsions can be made with nonionic, cationic or anionic surfactants. During this study, more than 200 different emulsions were made and tested for TCE degradation efficiency. A micrograph of one emulsion (Figure1(b)) shows that the nano-iron is contained within the aqueous phase of the micelle. Since the oil layer is the outer-most layer of the micelle, hydrophobic TCE is capable of dissolving through this layer and into the water/surfactant/iron phase where degradation takes place.

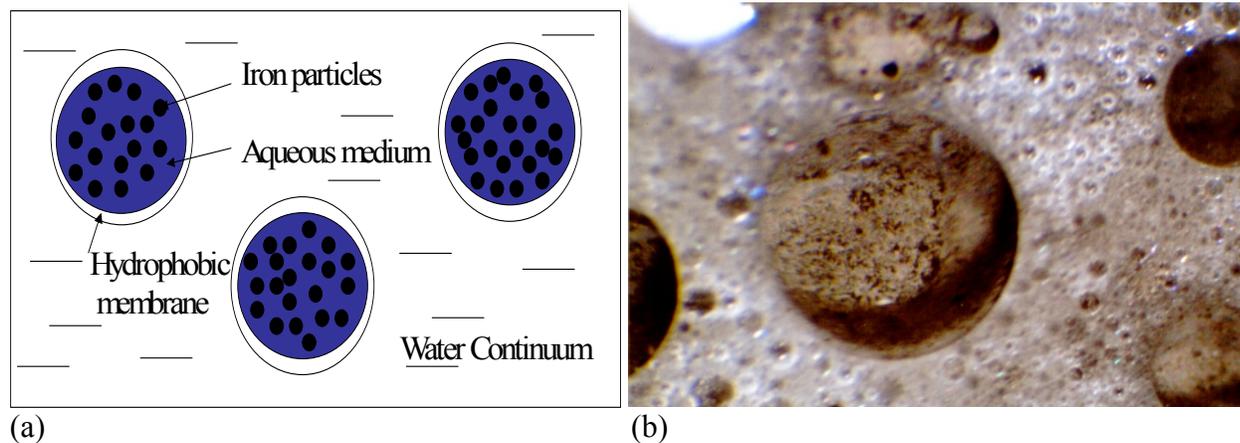


Figure 1. (a) Diagram of emulsion particle and (b) micrograph of nanoiron emulsion dispersed in water (magnification=1000X).

Kinetic studies were performed to determine the degradation efficiency of the various emulsions made in the lab. In order to quantify true destruction, ethene, the terminal product of the dehalogenation reaction, was measured by headspace analysis. Crimp-top, gas-tight vials were used for this work. All experimental work was carried out in an inert atmosphere glovebox. A measured amount (based on weight of iron) of emulsion was added to the vial along with deoxygenated, deionized water and 100- μ L of TCE. Each vial had five mL of headspace. Tests narrowed the most effective emulsions to those made with three surfactants, noted as surfactants A through C. These emulsions satisfied the practical need of being stable and flowable as well as

active. Experiments performed to test the efficiency of these blends for degradation of DNAPL TCE to ethylene revealed that five emulsions gave the best results and those are shown in Table 1. Surfactants A (blend 4) and C (blend 5) had the fastest reduction of TCE to ethene.

Table 1. Ethene (ppm) produced in the constant headspace vials (5-mL samples) over a 12-day period. Emulsions named by surfactant used.

<u>Emulsion Type</u>	<u>Day 1</u>	<u>Day 2</u>	<u>Day 3</u>	<u>Day 7</u>	<u>Day 12</u>
Surfactant A Blend #4	DL	6.15	8.91	19.32	38.06
Surfactant A Blend #5	DL	2.38	2.49	5.47	13.08
Surfactant B Blend #4	DL	4.03	6.21	10.29	14.69
Surfactant C Blend #4	DL	3.04	4.82	6.21	9.87
Surfactant C Blend #5	DL	7.04	9.92	28.94	33.88
Control	DL	DL	DL	DL	DL

None of the emulsions yielded concentrations of chlorinated by-products in solution above the detection limit (DL). The only product that could be measured was ethene and some small concentrations of other hydrocarbons. The chlorinated by-products produced during the degradation process (cis or trans-dichloroethene, vinyl chloride, etc.) remain in the emulsion and continue along the mechanistic pathways until ethene, a terminal product was formed. Ethene, which has a lower solubility in water (the interior phase of the micelle), exits through the micelle wall where it then enters free-phase water and the gaseous headspace. This is an important aspect of the use of such a technology since it does not release partially de-chlorinated byproducts to the groundwater. Further long-term studies are needed to clarify the lifetime usefulness of the emulsions. However, these early results indicate that free-phase TCE mass can be reduced quickly using this technique. Reduction of the source mass could significantly reduce remediation time and costs.

REFERENCES:

- Cahn, R.P. and Li, N.N., "Separation of Phenol from Waste Water by the Liquid Membrane Technique," *Separation Science*, Vol. 9, pp. 505-519, 1974.
- Kim, K.S., Choi, S.J., and Ihm, S.K., "Simulation of Phenol Removal from Wastewater by Liquid Membrane Emulsion," *Ind. Eng. Chem. Fundam.*, Vol. 22, pp. 167-172, 1983.
- Ruiz, N.E., "Application of Ultrasound to Enhance the Zero-Valent Iron-Initiated Abiotic Degradation of Halogenated Aliphatic Compounds," (Doctoral Dissertation), University of Central Florida, Orlando, Florida, 1998.
- Wang, C.B. and Zhang, W.X., "Synthesizing Nanoscale Iron Particles for Rapid and Complete Dechlorination of TCE and PCBs," *Environmental Science and Technology*, Vol. 31, No. 7, p. 2154, 1997.