

2002 NASA/ASEE SUMMER FACULTY FELLOWSHIP PROGRAM

**JOHN F. KENNEDY SPACE CENTER
UNIVERSITY OF CENTRAL FLORIDA**

NANOSCALE AND MICROSACLE IRON EMULSIONS FOR TREATING DNAPL

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ABSTRACT

This study demonstrated the feasibility of using emulsified nanoscale and microscale iron particles to enhance dehalogenation of DNAPL free-phase. The emulsified system consisted of a surfactant-stabilized, biodegradable oil-in-water emulsion with nanoscale or microscale iron particles contained within the emulsion droplets. It was demonstrated that DNAPLs, such as TCE, diffuse through the oil membrane of the emulsion particle whereupon they reach an aqueous interior and the surface of an iron particle where dehalogenation takes place. The hydrocarbon reaction by-products of the dehalogenation reaction, primarily ethene (no chlorinated products detected), diffuse out of the emulsion droplet. This study also demonstrated that an iron-emulsion system could be delivered in-situ to the DNAPL pool in a soil matrix by using a simulated push well technique. Iron emulsions degraded pure 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 systems can be injected into a sand matrix where they become immobilized and are not moved by flowing water. It has been documented that surfactant micelles possess the ability to pull pooled TCE into emulsion droplets where degradation of TCE takes place.

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1. INTRODUCTION

Remediation of chlorinated solvents in ground water is most commonly addressed using pump and treat technology. It is now widely recognized that due to the slow dissolution of solvents from residual or pooled dense non-aqueous phase liquid (DNAPL) sources, pump and treat primarily provides containment, rather than remediation. Because of this slow dissolution, pump and treat systems will need to be operated for long periods of time (i.e. decades or longer) in order to maintain protection of human health and the environment, incurring high operation and maintenance costs over that period.

Currently, there are no available proven technologies that can treat 100% of DNAPL sources (free-phase, residual phase, and sorbed [matrix diffused] phases). Attempts have been made to remove the DNAPL sources through heating to enhance volatilization (steam injection and radio-frequency-heating). This approach is limited because of the energy costs associated with heating the groundwater, and the exponential volume of areas that will need to be treated to ensure that the entire DNAPL source is encountered and treated. An alternative approach is to flood the source area with surfactants or oxidizing agents. This approach is also limited because the agents will move primarily through the most permeable zones, but considerable DNAPL mass will penetrate into areas of low permeability and will also diffuse (matrix diffusion) into geological materials. DNAPLs that exist in the matrix are dissolved or sorbed (2) and oxidizing agents can diffuse into the matrix and treat the dissolved NAPLs. Thus the very nature of DNAPL sources prevents complete removal that is required to prevent the remaining DNAPL from re-contaminating the groundwater.

There is a critical need for technologies that can effectively treat DNAPL sources in the saturated zone and result in both their destruction and containment with reduced treatment times and lower costs. This project addresses this need.

Significant work has demonstrated that zero-valent metals will reductively dechlorinate chlorinated DNAPLs such as trichloroethene (TCE) to ethene (3, 4). Permeable reactive barriers (PRBs) composed of iron have been shown to be effective in treating dissolved plumes of chlorinated solvents. Although this technology is passive and requires no energy, it still relies on the DNAPL dissolution and transport of dissolved chlorinated solvents to the PTW for treatment. Thus, the length of the treatment is not shortened and there is still a requirement for long-term monitoring. Insertion of iron into source zones by use of soil mixing technologies has been attempted, but this approach is limited to accessible sources, and by the depth of soil treatment. This research project addresses these limitations through the demonstration of an innovative technique that can be applied to DNAPL pools located under existing, occupied facilities and demonstrates the feasibility of using emulsified nanoscale iron particles to enhance dehalogenation of DNAPL free-phase.

The emulsified system consists of a surfactant stabilized oil-in-water emulsion with the nanoscale iron particles contained within the emulsion droplets. The surfactant serves two purposes: 1) it makes the emulsion stable for injection into the DNAPL and 2) the micelles within the emulsion droplet aid in the delivery of TCE to the iron. DNAPLs, such as TCE, diffuse through the oil membrane of the emulsion particle 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 a DNAPL pool through a series of push wells.

In the generation of the iron-emulsion system, it is desirable to use the smallest iron particles possible

because the small size produces a more stable and reactive emulsion that is capable of penetrating into the smallest of pore cavities between soil particles. Thus, it is desirable to use iron particles in the nanosize or microsize range. Microscale iron can be purchased from a variety of manufacturers. Nanoscale iron must be synthesized in the laboratory.

One of the methods used to synthesize nanoscale iron particles is to slowly add an aqueous solution of NaBH_4 to an aqueous solution of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$. The iron particles precipitate and can be readily separated from the solution (5). These chemicals are industrial chemicals produced in large quantities and are relatively inexpensive. A similar method for preparing nanoscale iron particles has been reported in the literature (6).

The nanoscale iron that has been prepared by this technique has a surface area between 15 and 25 m^2/g . This material has been demonstrated to be active in the dehalogenation of TCE in groundwater (7). Nanoscale iron could be mixed directly into water to form a slurry that could be injected into the ground to intercept or treat a plume of contaminated groundwater. However, if this aqueous slurry was to be used to directly treat a DNAPL pool, the hydrophobic pool would reject the hydrophilic slurry and thus the iron particles would not be delivered to the TCE molecules. 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 (8, 9). These liquid membranes are emulsion droplets that can be made to have a spherical hydrophobic skin and an aqueous hydrophilic interior. The iron particles are contained in the aqueous interior phase. The exterior of the droplet is hydrophobic and would be able to penetrate into a separate DNAPL phase. The chlorinated solvent would dissolve in the hydrophobic emulsion membrane and then move by diffusion into the aqueous interior. The dehalogenation reaction would then rapidly take place at the surface of the iron. A graphic rendition of what this system looks like at the microscopic level is shown in Figure 1.

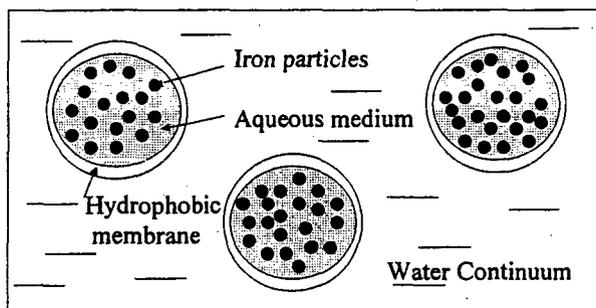


Figure 1. Nanoscale iron particles contained in emulsion droplet.

2. EXPERIMENTAL

Kinetic studies were performed to determine the degradation efficiency of the various emulsions made in the lab. In order to quantitate 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 (nitrogen) glove box. A measured amount

(based on weight of iron) of emulsion was added to the vial along with de-oxygenated, deionized water and 100- μ L of TCE. Each vial had five-mL of headspace. Analysis was performed using a purge and trap concentrator and a Trimetrics gas chromatograph equipped with a flame ionization detector.

Pumping Studies

A column experiment was set-up using 2-inch o.d. x 2.0 ft. length acrylic tubing and soil obtained from a research site at launch complex 34, Cape Canaveral Air Station, Kennedy Space Center, FL. The soil used was from a lower (26-40-ft. below land surface) sandy unit of a contaminated shallow aquifer. The porosity of the column material after packing was 32%. Water and emulsion was pumped into the column (vertical up-flow) at a rate of 65-ml per hour and a water:emulsion ratio of 5:1.

3. RESULTS AND DISCUSSION

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. Micrographs of a microscale iron emulsion (a) and a nanoscale iron emulsion (b) are shown in figure 2. The micrograph shown in Figure 2(a) was taken using a slide platform of depth approximately 200 μ m so the emulsion droplet wasn't flattened. Because the droplet was still spherical, some of the micro-iron appeared in focus and the iron near the top appeared out of focus. A nanoscale iron emulsion Figure 2(b) was examined using a standard microscope slide and cover slip so the spherical shaped droplet was flattened by the cover slip. It was obvious from both micrographs that the iron was contained within the interior of the droplets. Since the oil layer was the outer-most layer of the droplet, hydrophobic TCE can dissolve through that layer and into the water/surfactant/iron phase where degradation takes place.

Tests narrowed the most effective emulsions to those made with three surfactants: Rhodapon LSB (anionic, sodium laurel sulfate), Span 80 (neutral, sorbitan monooleate), and Span 85 (neutral, sorbitan trioleate). These emulsions satisfied the practical need of being stable and flowable as well as being active. Emulsions were then made in the blends shown in Table I.

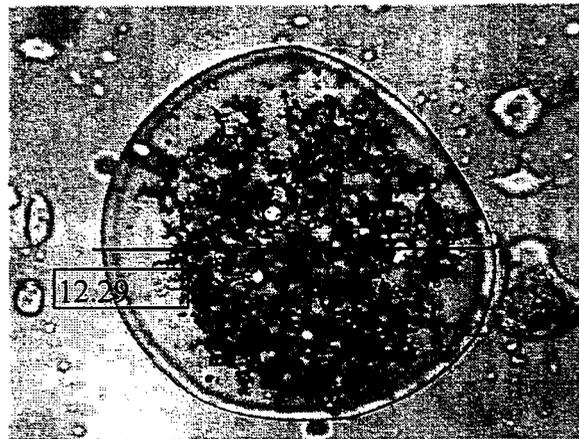
Table I. Composition of Emulsions Used in the Vial/Constant Headspace Kinetic Study.

<i>Emulsion</i>	<i>Nano Iron (wt%)</i>	<i>Corn Oil (wt%)</i>	<i>Water (wt%)</i>	<i>Surfactant (wt%)</i>
Blend #1	9.21	42.39	46.08	2.30
Blend #2	9.00	41.44	45.04	4.50
Blend #3	8.44	38.82	42.19	10.55
Blend #4	13.13	20.13	65.65	1.09
Blend #5	13.45	61.88	22.42	2.24
Blend #6	17.74	21.76	59.12	1.38

Experiments performed to test the efficiency of those blends for degradation of DNAPL TCE to ethene revealed that five emulsions gave the best results and those are shown in Table II. Rhodapon LSB (blend 4) and Span 85 (blend 5) showed the fastest reduction of TCE to ethene. Further long-term studies are needed to clarify the lifetime usefulness of the emulsions. However, these early results indicate that TCE mass in the DNAPL form can be reduced quickly using this methodology. Reduction of the source mass could significantly reduce plume remediation time and costs.



(a)



(b)

Figure 2. (a) Micrograph of a micro-iron emulsion dispersed in water. (b) Micrograph of nano-iron emulsion.

Table II. Ethene (ppm) Produced in the Constant Headspace Vials (5-mL samples) Over a 12-Day Period.

<i>Emulsion Type</i>	<i>Day 1</i>	<i>Day 2</i>	<i>Day 3</i>	<i>Day 7</i>	<i>Day 12</i>
Rhodapon	DL	6.15	8.91	19.32	38.06
LSB Blend #4					
Rhodapon	DL	2.38	2.49	5.47	13.08
LSB Blend #5					
Span 80	DL	4.03	6.21	10.29	14.69
Blend #4					
Span 85	DL	3.04	4.82	6.21	9.87
Blend #4					
Span 85	DL	7.04	9.92	28.94	33.88
Blend #5					
Control	DL	DL	DL	DL	DL

Note: DL denotes concentration below detection limit.

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. This indicates that TCE entered the emulsion and degradation occurred via proposed mechanisms (10). 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 is formed. Ethene, which has a lower solubility in water, exits through the droplet wall where it then enters free phase water and the gaseous headspace. This is an important aspect of the use of such a potential technology since it won't contribute to the pollution problem by allowing partially de-chlorinated by-products to enter the groundwater.

Pumping Studies

In preparation for field scale tests, practical properties of the emulsions had to be determined. A primary concern was how the emulsion could be pumped into the subsurface. To investigate this concern, a column experiment was set-up using 2-inch o.d. x 2.0 ft. length acrylic tubing and soil obtained from a research site at launch complex 34, Cape Canaveral Air Station, Kennedy Space Center, FL. The soil used was from a lower (26-40-ft. bls) sandy unit of a contaminated shallow aquifer. The porosity of the column material after packing was 32%. Water and emulsion (micro iron formulation #5) was pumped into the column (vertical up-flow) at a rate of 65-ml per hour and a water:emulsion ratio of 5:1.

After a period of four hours, the emulsion had passed through the length of the column and began exiting in the effluent. Samples of the effluent emulsion were examined under a microscope and verified that the emulsion did not break down through the pumping process. The column was then dismantled by cutting it in half along its vertical length. The emulsion had saturated the bottom one-half of the column and then found preferential paths through the remainder of the soil matrix.

A similar column experiment was carried out with nano-scale iron emulsion using the same formulation as the micro-scale iron emulsion used in the previous column experiment. The nano-scale iron emulsion flowed into and through the column more effectively and saturated the entire length of the column material. The emulsion exiting in the effluent was examined and found to be in droplet form. Soil samples

containing emulsion were also examined and the structure of the emulsion was retained.

Field Studies

In preparation for deployment of the pilot-scale injection of the emulsion, 400-gallons of emulsion were prepared at LC-34. An industrial scale mixer was used to prepare approximately 35-40 gallons in 55-gallon drums. Nanoscale iron, covered in de-oxygenated water and a nitrogen head was obtained from Toda America, Inc. and shipped to KSC in 55-gallon drums. Oil and surfactant was also obtained in drums. Water used for the emulsion was potable water obtained on-site. The formulation used was 70-100-36-3 of oil-water-iron-surfactant on a gram-weight basis.

Tests were conducted to determine the best available injection technique for emplacing the emulsion into the subsurface at depths up to 24-ft. bls. The tests took place at Launch Complex-34, Cape Canaveral Air Station, Florida during July 2002. Wavefront, Inc. (Canada) is the injection company chosen by the NASA, GeoSyntec, UCF team for deployment of the emulsion. The technology used involves low flow, high pressure pulses of emulsion injected into the matrix material followed by a water flush using the same parameters. The purpose of the water is to enhance the distance that the pulse can push the emulsion. The initial test of the technology revealed some engineering and mechanical problems that Wavefront had to re-address. The injection required a 5.5-hp pump instead of a 1.0-hp pump and the design of the injector and well plugs had to be changed. Even with these obstacles, 20-gallons of emulsion injected over a 3-ft section of well casing moved at least 12-inches from the well. It is assumed that due to the well plug problem that the emulsion probably short-circuited around the plug and back into the well casing. This would greatly reduce the amount of emulsion available for distribution into the soil matrix. Figure 3 shows a soil coring taken at 21-24-feet bls.



Figure 3. Core sample from 21 to 24 ft. bls. Distribution across end of core illustrates the distribution within soil matrix. Core tips (upper left) also show well-distributed emulsion droplets.

Micrographs of the emulsion recovered after injection show that the droplets withstood the pressure and shear forces of the injection process (Figure 4). This is important since the emulsion system is necessary

for DNAPL adsorption and degradation. If the droplets were destroyed in the injection process, only solubilized chlorinated hydrocarbons would be treated by this method.

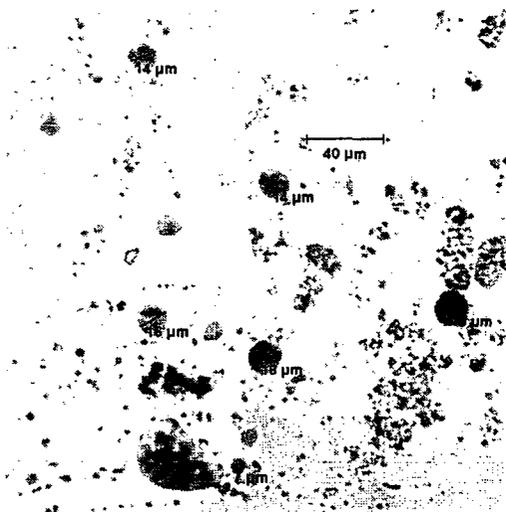


Figure 4. Micrographs of emulsion droplets from two different corings after field injection.

3. CONCLUSIONS

Emulsions containing microscale and nanoscale iron have been developed and tested at the University of Central Florida Chemistry Department. The components of the emulsion, corn or vegetable oil, food-grade surfactant, water and iron particles are biodegradable and/or harmless to the environment. These emulsions have been shown to encapsulate and degrade DNAPL in both water and soil matrices. Chlorinated by-products of the degradation of TCE are not released from the emulsion in measurable quantities. Ethene, a non-chlorinated product of the reaction, can be quantified and was used to follow the rate of the degradation reaction. The emulsion can be pumped at pressures of 160-psi in laboratory experiments through fine-grained or more coarse-grained materials. A field injection test showed that a direct push injection technology is not adequate for subsurface placement of the emulsion. Other technologies are being evaluated.

A field test that is being evaluated under the US EPA SITE (Superfund Innovative Technology Evaluation) Program is currently underway at Cape Canaveral Air Station, Launch Complex 34. This NASA cleanup site has been extensively characterized and it is estimated that over 40,000 kg of DNAPL (TCE and cis-DCE) lie beneath a former parts cleaning facility on the site.

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