EVALUATING THE DISTRIBUTION OF EMULSIFIED ZERO-VALENT IRON FOR FOUR DIFFERENT INJECTION TECHNIQUES

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ABSTRACT: Considerable attention has been devoted in the past few years to research and field-application of source treatment technologies, as they have the potential to lower the overall cost and time required for remediation of contaminated aquifers. In 2002, a small-scale field pilot test of emulsified zero-valent iron (EZVI) was conducted under the NASA STTR program and the US EPA SITE program to assess the ability of this technology to treat a TCE DNAPL source zone. The pilot test, conducted by NASA, GeoSyntec and the University of Central Florida showed promising results as a method for significantly reducing both mass and mass flux from DNAPL source zones. However, additional field demonstration research was deemed necessary to improve the EZVI subsurface delivery approach. This paper presents the data collected from an EZVI injection demonstration conducted in January 2004 that tested four different injection technologies.

EZVI HISTORICAL OVERVIEW

Significant laboratory and field research has demonstrated that zero-valent metals will reductively dehalogenate dissolved chlorinated solvents such as tetrachloroethene (PCE) and trichloroethene (TCE) to ethene. Permeable reactive barriers (PRBs) containing zero-valent iron as the reactive material have been shown to be effective in treating plumes of dissolved chlorinated solvents. PRB technology is passive and requires no energy; however, it still relies on DNAPL dissolution and transport of dissolved chlorinated solvents to the barrier for treatment, and therefore PRBs do little to reduce the clean-up time for the site.

EZVI can be used to enhance the destruction of chlorinated DNAPL in source zones by creating contact between the DNAPL and the nano- or micro-scale iron particles. EZVI is composed of food-grade surfactant, biodegradable oil, water, and zero-valent iron particles (either nano- or micro-scale iron), which form emulsion droplets that contain the iron particles in water surrounded by an oil-liquid membrane. Figure 1 includes a schematic and a magnified image of an emulsion droplet. Since the exterior oil membrane of the emulsion particles have similar hydrophobic properties as DNAPL, the emulsion is miscible (i.e., the phases can mix) with the DNAPL.

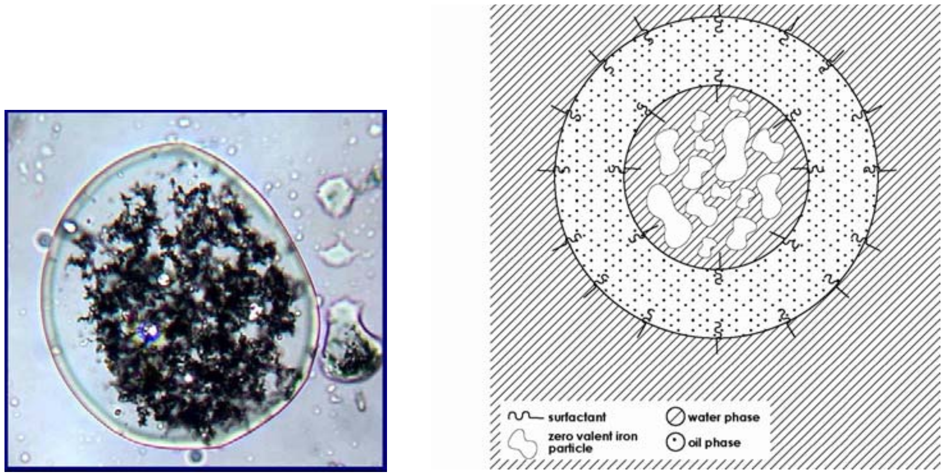

Figure 1: Magnified image and schematic of emulsion droplet

2004 FIELD TEST OBJECTIVES

The first field demonstration for EZVI was conducted at NASA's Launch Complex 34 on Cape Canaveral Air Force Station in Florida. Pressure pulsing technology (PPT) was used to distribute EZVI beneath the site's Engineering Support Building within a 9 X 15 ft plot at a depth of 16-26 ft below the foundation. The test revealed inconsistent distribution of EZVI within the target zone. Results of the post-demonstration coring led to the conclusion that the three to four ft depth interval over which injection was occurring led to fingering and short circuiting of the EZVI to depths above the target zone. In an effort to test this hypothesis and to test the capabilities of other possible injection techniques, NASA initiated another field-scale deployment of EZVI in January of 2004. The purpose of the 2004 field test was to evaluate the ability of pneumatic injection, hydraulic injection, direct push injection and PPT over a narrower depth interval to evenly disperse EZVI over a projected radius of influence (ROI) and to achieve less than a 50 percent saturation of EZVI within this ROI.

GeoSyntec sub-contracted four vendors (Pneumatic Fracturing, Inc. (PFI), Wavefront Energy and Environmental Technologies (Wavefront), Vironex, and FRx, Inc.) to demonstrate their technologies ability to emplace EZVI at two depth intervals (15 to 16 feet below grade (bg) and 18 to 19 feet bg). Approximately one hundred gallons of EZVI was provided to each vendor and they were allowed to use water, nitrogen and guar as co-injection fluids. Each technology's performance was evaluated on the following criteria:

- the ability to distribute the EZVI in an even and controlled manner out to a distance of 5 to 7 ft from the injection point;

- the ability to control and maintain the EZVI distribution out to the edge of the radius of influence over the target injection depth intervals between 15 – 16 ft below ground surface (ft bgs) and/or 18 – 19 ft bgs; and
- the ability to control the direction of the injection if this is something that a specific technology has the ability to control (i.e., inject over only a 90° radius from the injection point rather than create a "cylinder").

Prior to field activities, NASA supplied the pneumatic (PFI) and hydraulic (FRx, Inc.) injection vendors with EZVI to demonstrate that their technology would not damage the EZVI in a bench-scale test. PFI completed the bench-scale testing in November 2003 and FRx in January, 2004. Neither technology appeared to compromise the emulsion droplets based on bench scale tests.

FIELD SET-UP

Four distinct injection locations were selected along a hedge line at Launch Complex 34. Figure 3 illustrates the locations and the subsurface lithology at the target depth. In order to monitor for the presence of EZVI, soil cores were collected after each vendor's injection at varying radii from the injection point. Two FLUTe® Liners were also installed at 3.5 feet out from the injection point for each technology location as a qualification detector of NAPL.

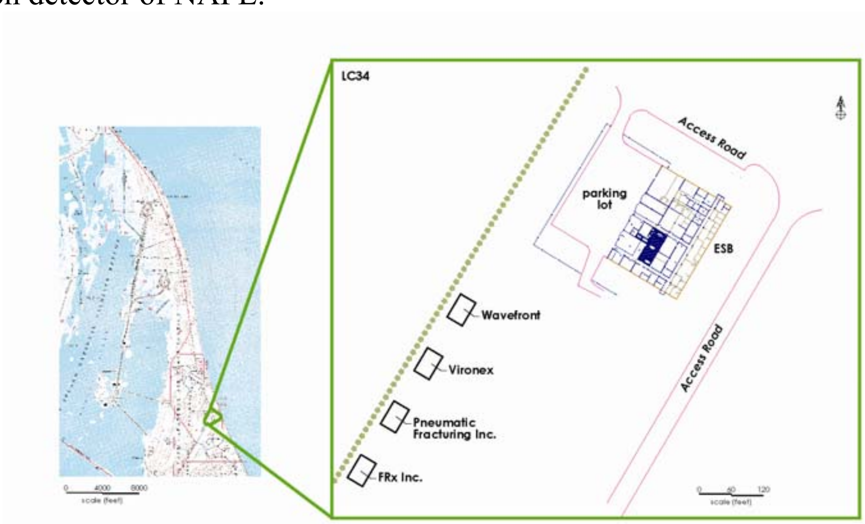

Figure 2: Injection Testing Locations

PNEUMATIC INJECTION

PFI utilized nitrogen as the pneumatic fracturing and carrier or co-injection fluid. The nitrogen arrived at the site on a semi-trailer tube bank. A two-step pneumatic injection procedure was conducted at this site. First, the formation was fluidized, followed by EZVI injection. The injection nozzle, which is bullet shaped, is designed to inject media in a horizontal or planar format in a 360° circumference. The nozzle itself is directional, so that each injection covers an area of 90°. To achieve a 360° circumference, the nozzle can be rotated between injections. After the 360° of injection has been completed, the nozzle is retracted upwards and the process is repeated. (PFI, 2004)

For this project, PFI originally projected that two injection directions would be completed per injection depth (a 180 degree arc) and two depths would be targeted within the one-foot depth interval (i.e., 18 to 19 feet and 15-16 feet bgs). Therefore, a 90 degree injection radius would be achieved at a single target depth with two injections at 18.5 to 19 feet bg and 18 to 18.5 bg. Once the one-foot depth interval was completed, the nozzle would be retracted to 16 feet bgs and the process repeated. In the end, only one depth was targeted (18-19 feet bgs) due to time constraints.

Actual EZVI injection pressures ranged between 40 and 55 psi. The nitrogen starting and ending pressures ranged between 1500 and 2000 psi. The elapsed time to inject 15 gallons in a single direction was 430 seconds or approximately seven minutes. Figure 4 contains illustrative photos of the injection apparatus used during the field demonstration.

Confirmation sampling indicated that based on visual observation, the minimum radius of influence achieved by pneumatic injection was 3.5 feet. Somewhere between 4.0 and 4.5 feet is the speculated ROI for this test. In Direction No. 2, some EZVI was visually observed at 4 feet. Based on confirmation sampling, it was determined that the original direction of the nozzle for the first injection was not towards Direction No. 1 but actually in Direction No. 2 (see Figure 3). PFI inadvertently pumped EZVI during the rotation of the nozzle and injected a total of 80 gallons of EZVI along a 270 degree arc behind the target injection zone.

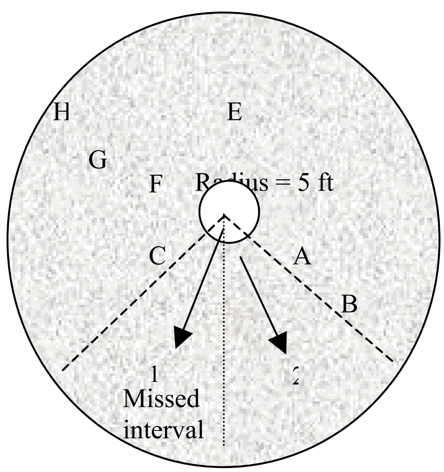

Figure 3: PFI Injection and Sample Locations

Analysis of the soil collected post-injection showed no evidence of emulsion droplet deformation or destruction caused by the actual field injection process. EZVI saturation of the soil column at the target depth was visually confirmed using soil cores. No FLUTe® Liners were installed at this location. Instead, additional soil cores were collected. EZVI was visually confirmed to be distributed within the target depth along the 270 degree arc at a thickness ranging from six to eight inches.

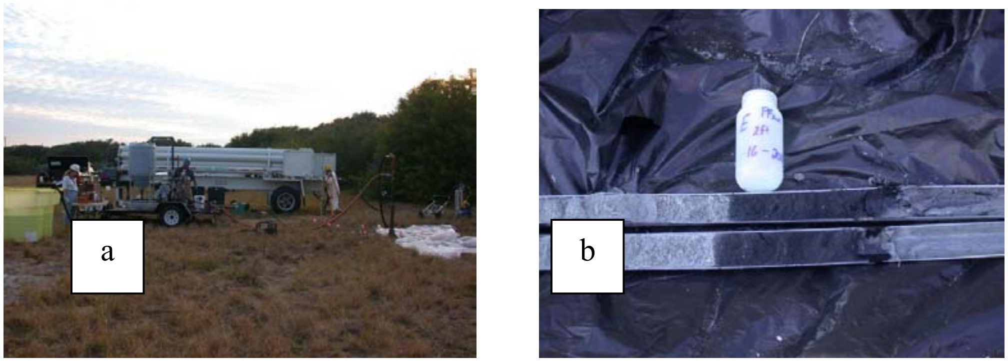

Figure 4: a) Pneumatic Injection of EZVI Setup and b) Soil Core Findings

HYDRAULIC FRACTURING

FRx generated a hydraulic fracture at Launch Complex 34 using the following approach (FRx, 2004):

- Installed a dedicated well consisting of a 2-inch pipe (GeoProbe® rod) fitted with a drive point;
- Open a short section of open hole by withdrawing the pipe upwards a few centimeters;
- Cutting a thin notch in the wall of the borehole by means of a horizontal hydraulic jet;
- Pressurizing the notch with liquid so as to nucleate a horizontal fracture from its outer edge;
- Delivering fracturing fluid to the open hole section of the well so as to propagate the fracture; and
- Monitoring the injection pressure and surface deformation, which permited deduction of the fracture form.

Notching was done with a guar gel solution pressurized to ~20 MPa. This process generated approximately 2.5 gallons of slurry composed of soil cuttings suspended in guar solution. Borax cross linker was delivered to the well to aid in removal of the cuttings. After cutting the notch, the nozzle was raised to be within the well, and the well was purged of notch cuttings by delivery of cross linked gel.

After notching operations, the well was attached to a positive displacement pump. Initially the pump was charged with 45 gallons of cross linked guar gel. The guar gel was injected to nucleate the fracture and propagate it to an extent and aperture that would permit entry of EZVI without extensive shear. After injecting the cross linked guar gel, the pump was paused while the hopper was charged with EZVI. About 100 gallons of EZVI were injected.

During injection, well head pressure was observed and recorded manually. An array of uplift measurements was made at 5.0, 10, and 4.5 ft from the injection well along six directions. The initial pressure for both guar and EZVI increased to about 480 kPa and then gradually decreased toward 300 kPa. No uplift or heaving was noted during the injection process.

Several hours after creation of the fracture, two NAPL FLUTe® liners were installed in borings 5 ft west and 5 ft south of the injection well. The liners were left in contact with the formation for at least 1.5 hours. No staining was noted on the liners. In addition to the FLUTe liners, several cores were collected. No evidence of EZVI was noted visually in three cores collected at radiuses of up to 5 feet from the injection point. A thin lens containing EZVI was recovered from a core taken 2 ft south of the injection at 18 ft bgs. Evaluation of the EZVI found in the one core did clearly indicate that the injection process did not damage the emulsion droplet. Figure 5 shows the hydraulic fracturing injection nozzle and field set up.

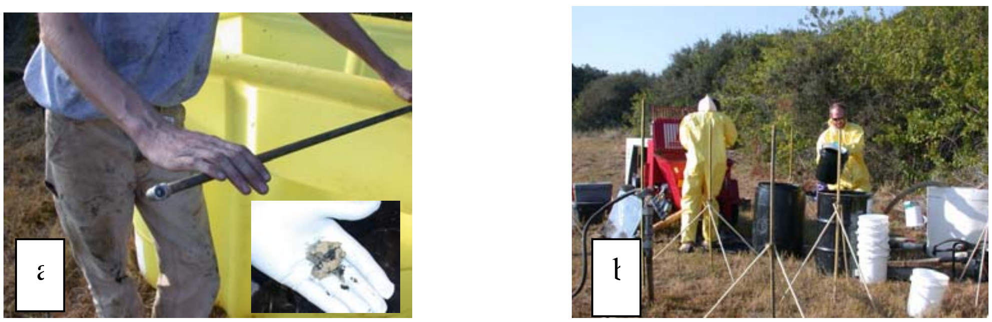

Figure 5: a) Hydraulic Fracturing Injection Nozzle showing fracture visually seen in a core sample and b) field injection setup.

PRESSURE PULSED INJECTION

EZVI was injected by Wavefront using PPT. This technology involves injecting fluid while simultaneously applying large-amplitude pulses of pressure to porous media at the water table or variable depths. These pressure pulses cause instantaneous dilation of the pore throats in the porous media, and thus increase fluid flow (Battelle, in Press).

PPT uses a process of periodic large-impulse hydraulic excitations to introduce hydraulic strain energy into the formation. Applied to geologic formations exhibiting elastic properties, this energy opens perforations, increases pressure, and generally enhances the ability to move fluids. High-amplitude wave pulses are generated by blasts of air delivered by a proprietary pneumatic system. The air is used to drive down a piston in the well head assembly that transmits the pressure pulse to the fluid contained in the injection tool and well. Pulse rate and amplitude are calculated based on site parameters. A porosity-pressure pulse propagates at between 5 and 300 m/s (15 to 900 ft/s) depending on the fluid viscosity, permeability, and the scale of the pulse. Mechanical energy capture causes a buildup of pressure in the reservoir, deforming the material elastically outward (Battelle, in Press).

For this test, Wavefront was given 100 gallons of EZVI, with the goal of injecting it in five stages. Each stage would involve the injection of 20 gallons of EZVI, followed by 40 gallons of water. After all the EZVI was injected, additional water would be injected until the total amount of injected water corresponded to a 10:1 ratio with EZVI. The staged injection would periodically disperse the EZVI with water, resulting in better coverage and reducing the risk of damage to the well caused by high pressures (Wavefront, 2004).

The first 25 gallons of EZVI and 40 gallons of water went into the target depth of 15-16 ft bgs utilizing injection pressures of up to 20 psi. The second injection delivered

20 gallons of EZVI and 30 gallons of water at pressures up to 27 psi. During initiation of the third EZVI pulsing, EZVI was noted to be coming up around the already installed FLUTe® line, 3.5 ft from the injection well. No further injection attempts were made. The tooling was dismantled and soil core samples were collected. Figure 6 depicts the injection equipment used and shows the evidence of EZVI coming up along side the FLUTe® liners.

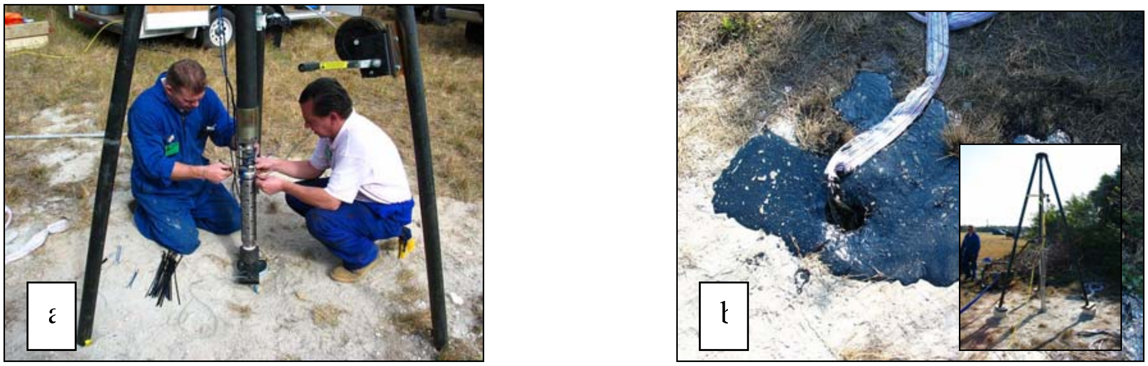

Figure 6: a) PPT tooling with lower pneumatic packer already installed and injection holes visible. b) Evidence of EZVI coming up the FLUTe® liner on the far side of the tool.

EZVI was found in one soil core approximately 2 ft from the injection point and traveled 3.5 ft from the injection port in the direction of the flute liner where it short circuited to surface. The EZVI was well distributed within the soil core at 2 ft from injection; however the EZVI was only observed at a depth of 7 ft bgs as opposed to the targeted 15-16 ft bgs. The second FLUTe® liner confirmed the presence of oil at the target depth, but no EZVI was visible in the soil samples collected near this liner even under the microscope.

After reviewing the data with Wavefront, the following explanation is hypothesized: PPT relies on the installation of a standard well whose borehole is typically sealed using bentonite chips or grout. The well at LC34 was installed for 10 days prior to EZVI injection and therefore may not have had sufficient for the well seal to set up enough to handle the PPT injection pressures. EZVI most likely traveled up the well boring and found a path of least resistance at 7 ft bgs, still below the water table. Although the well was installed using careful installation practices, future installation may necessitate using concrete for the borehole seal, to minimize the potential for EZVI short circuiting along the borehole.

DIRECT PUSH INJECTION

Vironex Inc. has installed EZVI at LC34 using their direct push equipment on two occasions (2003 and 2004). Their previous injection distributed the EZVI directly at the targeted depth, and was able to displace it radially out from the injection rod approximately one foot. In an effort to enhance this radius of injection, Vironex deployed a 1000W submersible ultrasound transducer that resonated between 330 and 360 hertz into a well placed five feet from the injection location. For one hour prior to, and during EZVI injection, the transducer emitted sonic waves in an effort to enhance

EZVI distribution in the direction of the transducer. Vironex also injected EZVI through their direct push rod without the use of ultrasound using water as a co-injection fluid.

The results from this injection testing are unavailable at the time of this paper's submission deadline, but will be presented during the conference.

INSTALLATION SUMMARY

Pneumatic injection clearly showed promise for application to sandy soils. The technology placed EZVI in the target depth over a six-inch thick interval out to a radius of four feet. The only negative encountered during the testing was that EZVI was lost behind the intended injection direction when the nozzle was rotated and the pump was left on, leaving insufficient EZVI to determine the maximum radius of influence. This question is being further explored by PFI in the laboratory. Additionally, pneumatic injection appears to nearly saturate the pore spaces with EZVI at the target depth, resulting in higher than necessary concentrations of EZVI in the target interval. The ability to "thin out" the distribution is also being evaluated by PFI in the laboratory.

The use of hydraulic fracturing in unconsolidated sediments was clearly a long-shot. The inability to locate EZVI after the injection was puzzling, but not unexpected. The cross-link gel was intended to open the formation for short period of time so that the fracture might initiate where intended, however the flowing sands may not have "propped open" and the formation may have collapsed. It was indeed lucky to find even a trace of the emulsion using the soil coring inspection technique, and so what was gained from the hydraulic fracture testing was that the process does not harm the emulsion structure and therefore it may have significant application to more consolidated lithologies.

Pressure pulsing technology provided good distribution of EZVI within the soil structure. The lenses encountered were not fully saturated with EZVI and the travel distance was over 3.5 feet from the injection well. However, the technology may be very sensitive to well installation and preferential flow paths. Short circuiting up the borehole may have precluded this technology's demonstration from transporting EZVI laterally as intended, as the commodity rose up along the borehole until it found a highly transmissive zone around seven feet below grade.

Direct push technology certainly has potential application to small DNAPL sites. Direct push rigs can be rented by the day and many small "column's of EZVI" placed within the impact zone in a single day. Because EZVI is a passive technology, after injection no further operations are necessary. This would seem particularly attractive to the dry cleaner programs across the United States.

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