GeoSyntec Consultants

UCF

Reductive Dehalogenation of DNAPLs Using Emulsified Zero-Valent Iron

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Performance Evaluation of Emulsified Zero-Valent Iron (EZVI)

- **GeoSyntec and the University of Central Florida (UCF) are evaluating EZVI to treat a TCE DNAPL source area at Cape Canaveral, FL**
- **Evaluation is funded by a NASA STTR grant**
- **Performance evaluation is being simultaneously validated by USEPA Superfund Innovative Technology Evaluation (SITE) Program**
- **Performance evaluation involves laboratory testing and a pilot-scale field demonstration to be conducted interior to the engineering services building (ESB) at Launch Complex 34 (LC34)**

Summary of EZVI Technology

- EZVI is composed of surfactant, biodegradable oil, water and zero-valent nano-scale iron particles which form an emulsion of fine droplets or micelles (Figure 1)
- EZVI enhances destruction of DNAPL by creating intimate contact between DNAPL and nano-scale iron particles
- Exterior oil membrane of micelles have similar hydrophobic properties as DNAPL and therefore emulsion miscible with DNAPL
- TCE diffuses through oil membrane of micelle and undergoes reductive dechlorination facilitated by zero-valent iron (Figure 2)
- While iron particles remain active, TCE continually degrades within micelle, maintaining concentration gradient across the oil membrane, the driving force for TCE migration into micelle
- Final by-products (non-chlorinated hydrocarbons – i.e. ethene) diffuse back out of micelle into surrounding water

Figure 1: Schematic of Micelle Structure of the Emulsified Zero-Valent Iron EZVI Pilot Demonstration

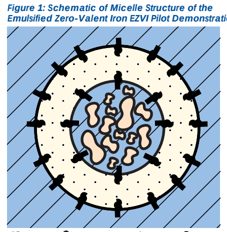
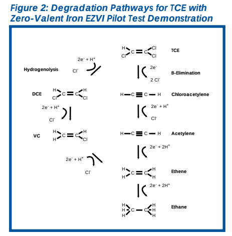


Figure 2: Degradation Pathways for TCE with Zero-Valent Iron EZVI Pilot Test Demonstration



Laboratory Studies Conducted at UCF

- Initial lab tests demonstrated that EZVI could be delivered to a pool of DNAPL in a soil matrix and was able to degrade DNAPL while non-emulsified ZVI particles were non-reactive with the DNAPL
- Tests were run with both micro-scale (Figure 3a) and nano-scale iron particles (Figure 3b).

Figure 3a: Micrograph of a micro-iron emulsion

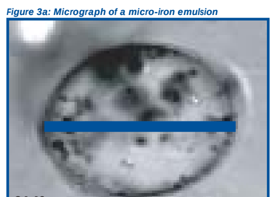
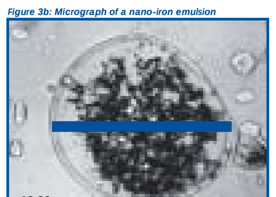


Figure 3b: Micrograph of a nano-iron emulsion



Laboratory Studies Conducted at UCF

- Smallest iron particles size possible produces a more stable and reactive emulsion that is capable of penetration in to smallest pore openings in porous matrix
  - Micro-scale iron can be purchased from various manufacturers
  - Nano-scale iron must be synthesized in the laboratory or purchased from foreign manufacturer
  - Nano-scale iron particles synthesized by slowly adding an aqueous solution of $NaBH_4$ to and aqueous solution of $FeCl_3.6H_20$; iron particles precipitate and can be separated from solution
- Micrographs were taken of an emulsion made with water that was dyed green to show the different fluid phases (Figure 4).

Figure 4: Nano-iron emulsion made with green dyed water dispersed in undyed water

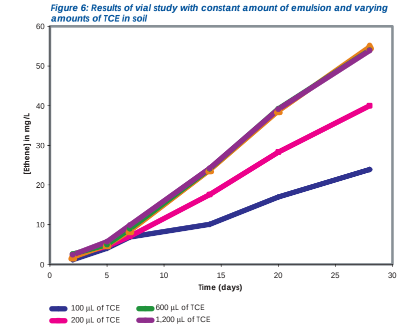
Figure 5a: Column studies in laboratory

Figure 5b: Emulsion being pumped through column

- Additional lab tests conducted to optimize emulsion formulations
  - Emulsions were created using different biodegradable oils and surfactant in varying concentrations and with various emulsion preparation procedures.
  - Stability, mobility and physical properties of each emulsion was evaluated
- Vial and column tests were conducted to test reactivity, stability and "pumbability" of emulsion (Figure 5a & b)

- Emulsion was successfully pulse pumped through columns packed with sand from LC34 but was difficult to pump (pressures as high as 160 psi).
- Micrographs of emulsion were taken of effluent to confirm that micellular structure maintained
- A variety of vial studies were conducted to test the efficiencies of the emulsions made
  - Chlorinated by-products were not detected in the headspace of any of the emulsion experiments
  - Only ethene by-products and small concentrations of other non-chlorinated hydrocarbons by-products were measured
  - If emulsion was sonicated to break up the micelles, cis 1,2-DCE and VC were detected
  - Iron consumption studies were conducted by adding varying amounts of TCE in soil and measuring the production of ethene (Figure 6)

Figure 6: Results of vial study with constant amount of emulsion and varying amounts of TCE in soil

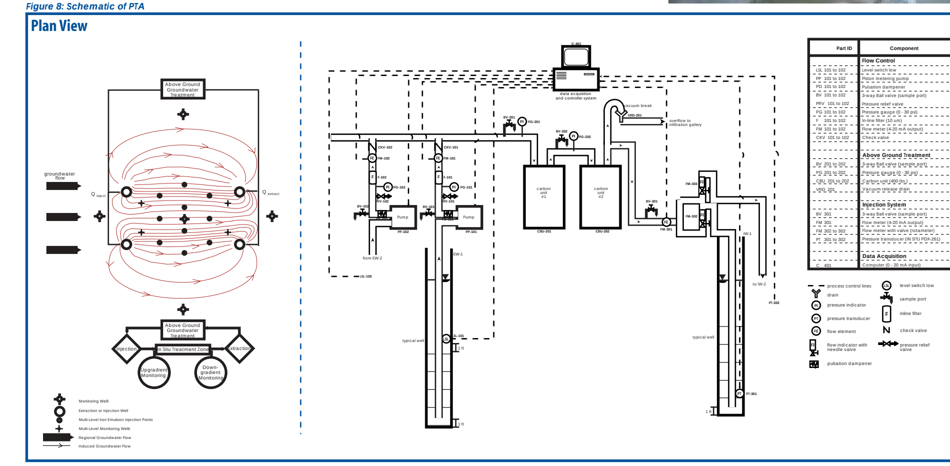


Field Demonstration

- LC34 former launch site for Saturn rockets from 1960 to 1968
- Chlorinated solvents, including TCE, used to clean rocket engines inside and outside of ESB
- Documented presence of DNAPL beneath the building
- DNAPL distribution in vicinity of pilot test area (PTA) characterized by taking 8 cores and extracting them with methanol to get estimates of TCE mass
- Based on results of coring the PTA is 9.6 x 15 ft in area with a target depth interval for treatment from 14 to 24 ft bgs
- PTA hydraulically controlled for containment and to maintain consistent groundwater velocity in treatment zone (Figure 7, Figure 8)

Figure 7: Photo of recirculation system at PTA

Figure 8: Schematic of PTA



EZVI Injection Testing

- Scale up emulsifying process from lab scale to field scale (Figure 9)
- Based on lab tests, decided that pumping emulsion into the ground through wells would not be feasible
- Considered injecting EZVI within PTA in a grid pattern using a direct push technique through drive point
  - Tested injection method in the field and found most of the emulsion short circuited up borehole (Figure 10)
  - Radius of influence small and channeling likely
- Now considering other injection techniques
  - Inject EZVI with a low pressure, high velocity nitrogen "carrier" through pneumatic injection techniques
  - ARS Technologies Inc. testing emulsion to see if nitrogen can work as an effective carrier (Figure 11a & b)
  - Also considering using a pressure pulse technology to distribut EZVI from wells
  - Wave Front is now testing pressure pulse methods of distributing EZVI

Figure 9: Field scale emulsifier

Figure 10: Injection tests with direct push rig

Figure 11a: Emulsion being hydraulically pumped through injection nozzle

Figure 11b: Emulsion being atomized by nitrogen carrier gas

Technology Open House

- Interested parties are invited to come & learn about two technology demonstrations (Bioaugmentation & EZVI)
- Tentative date for open house at Cape Canaveral November 7, 2002