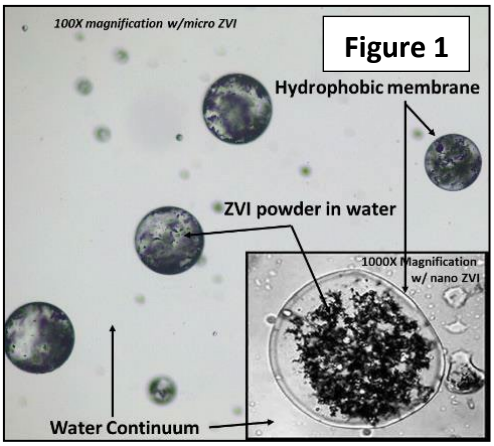
ADVANCED EZVI FORMULATIONS FOR THE REMEDIATION INDUSTRY

Provectus Environmental Products, Inc. offers the most advanced, cost-efficient formulations of the NASA patented emulsified zero valent iron (EZVI) technology to the remediation industry. Millions of pounds of EZVI have been used successfully at locations throughout the United States (including Superfund sites), Canada, France, and Australia (Reinhart, 2003; Su et al., 2017). Provectus' scientists have unmatched experience and expertise with practical formulation, manufacturing, design, and full-scale technology applications.

Provectus' EZVI formulations (**Figure 1**) uniquely provide:

- **Controlled methanogenesis** – safer, more efficient, more effective and used on a site-specific basis
- **Lower viscosity** formulations – maximizes subsurface distribution and contact
- **pH stabilized** formulations – optimizes emulsion stability and reactivity
- **Catalyzed ZVI** – enhances reactivity by augmenting electron transfer processes



Additional benefits of our EZVI product offerings include:

Technical

- Quality assured products
- Emulsion structure, density, hydrophobicity
- Proven effectiveness and longevity
- Custom formulations available
- NASA Patents Recognized and Honored

Economic

- Competitive in situ DNAPL and source destruction technology
- Green & sustainable product
- Made in the USA (FAR 52.225-11)

INTRODUCTION

The remediation of a dense non-aqueous phase liquid (DNAPL) is complicated by its physical and chemical properties (EPA, 2004). By definition, DNAPLs are compounds that have specific gravities greater than water (>1 g/cm^3), low water solubility, and therefore, a hydrophobic physical chemistry. The presence of DNAPL at a site can act as an ongoing source of contaminant to groundwater for decades. Chlorinated solvents are present as DNAPLs at many Superfund sites (EPA, 2004). The potential effectiveness of ZVI for remediation of groundwater impacted by chlorinated solvents has been documented since the early 1990s (Gillham, 1994). As described by Arnold and Roberts (1998), chemical transformation via ZVI occurs on particle surfaces and therefore involves at least three steps: (a) adsorption of the substrate to reactive sites on the ZVI

particle surface, (b) reaction at the surface, and (c) desorption of the transformation product. In the absence of interspecies competition by catabolites, the kinetics of PCE transformation via α- and/or β-elimination reactions (and, to a lesser degree, hydrogenolysis and hydrogenation reactions) is therefore directly related to reactive surface area.

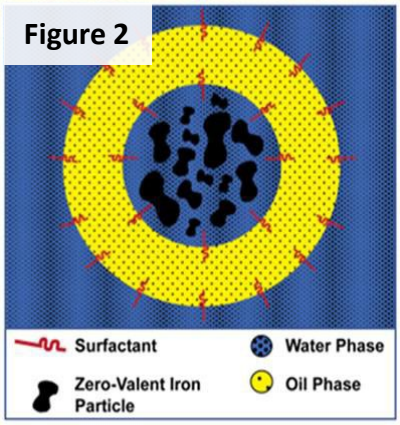
The ZVI mediated transformation processes described above are relevant for dissolved phase contaminant destruction, as the ZVI requires a hydrogen donor for the abiotic reactions to proceed (Brown *et. al.,* 2009). Because DNAPL is not in the dissolved phase and has a hydrophobic physical chemistry, injection of ZVI slurries into source areas will not provide direct destruction of source material. The EZVI technology provides a solution to this problem and is engineered to enable maximum contact with source materials, while including ZVI suspended within water so that direct DNAPL destruction is possible using the ZVI technology.

ZVI PLUS VEGETABLE OIL IS NOT EZVI

Emulsion Structure

EZVI combines food grade vegetable oil (VO) with a surfactant, elemental iron, and water in a specific physical structure to enable direct DNAPL destruction utilizing a combination of abiotic and biotic processes. The key innovation surrounding the EZVI technology is the structure of the emulsion (Quinn *et al*., 2005, Su *et al*., 2017). In order for the NASA patented technology to perform as designed, the emulsion structure, which is a water-in-oil type emulsification, must be in place (see **Figure 2**). The structure of the EZVI technology enables:

- Miscibility with DNAPLs in situ
- Continuous sequestration (phase partitioning) of chlorinated solvent into outer VO membrane (decreased contaminant mass flux)
- Encapsulates ZVI so that it targets only COIs with hydrophobic physical chemistry
- Provides slow-release hydrogen source for biostimulation downgradient of source area



DNAPL treatment with EZVI proceeds via 3 primary steps:

- Sequestration (into outer lipophilic membrane)
- Dissolution (into interior aqueous phase)
- Reductive dehalogenation (utilizing abiotic and biotic processes)

Miscibility with DNAPLs

Due to the above structure, the EZVI technology is itself a DNAPL. The outer vegetable oil membrane provides matching hydrophobic physical chemistry such that the remedial emulsion is fully miscible with contaminant of interest (COI) source material in situ (see **Figure 3**). This unique characteristic enables maximum contact with DNAPL materials *in situ*, which is critical to accomplish direct source material destruction.

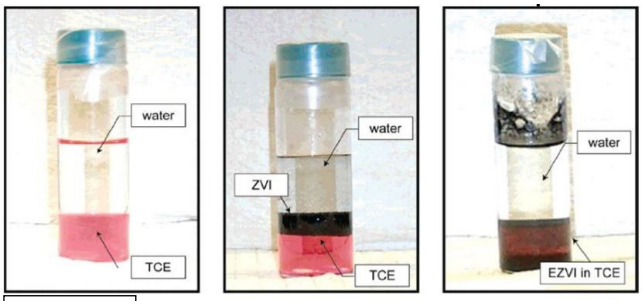


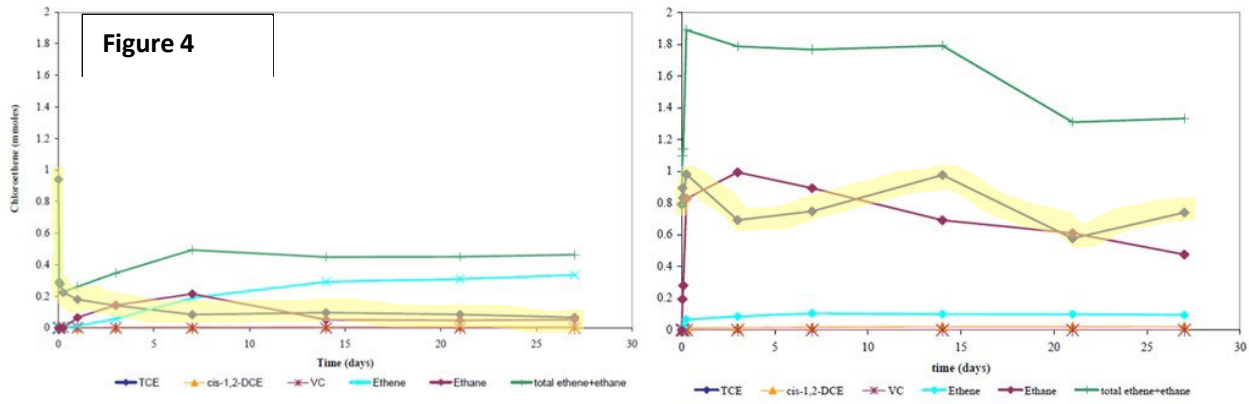
Figure 3

Miscible with DNAPL
Ref: Brooks et al., 2000

Decreased Source Area Mass Flux

When the EZVI technology is implemented within a source area, the chemical equilibrium is disrupted and hydrophobic contaminants (e.g., chlorinated solvents) phase partition into the vegetable oil membrane of the emulsion. By emplacing this lipophilic membrane within the source area, the water solubility of the hydrophobic contaminants is effectively decreased, see **Figure 4**, where the EZVI microcosm demonstrated a 90% decrease in dissolved TCE concentrations, while the ZVI microcosm showed little change in dissolved TCE concentrations. This is the result of rapid phase partitioning or sequestration of the DNAPL into the outer membrane of the emulsion, and results in dramatically reduced groundwater concentrations which in turn provide significant reduction in contaminant mass flux from an EZVI treated source area.

Figure 4



EZVI and KB-1 DNAPL **ZVI and KB-1 DNAPL**

Ref: O'Hara et al., 2005

Combined Technologies Abiotic and Biotic Processes

Abiotic reductive dehalogenation processes primarily occur on the interior of the emulsion where the highly reactive ZVI powder is encapsulated with water. This creates a COI concentration gradient across the lipophilic membrane into the interior of the micelles, and continually pulls

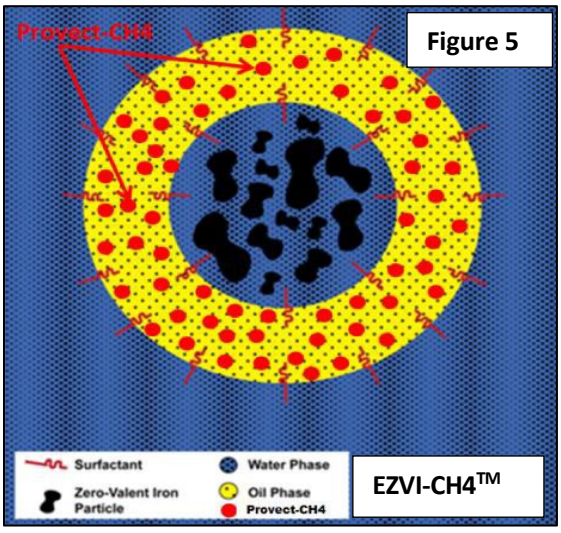
contaminant mass into the emulsion. The biologically mediated processes are primarily occurring on the outside (exterior) of the emulsion and downgradient (hydraulically) from the treated source area. The outer membrane is a fermentable substrate (vegetable oil) that provides hydrogen for the microbes to utilize, creating biostimulated conditions.

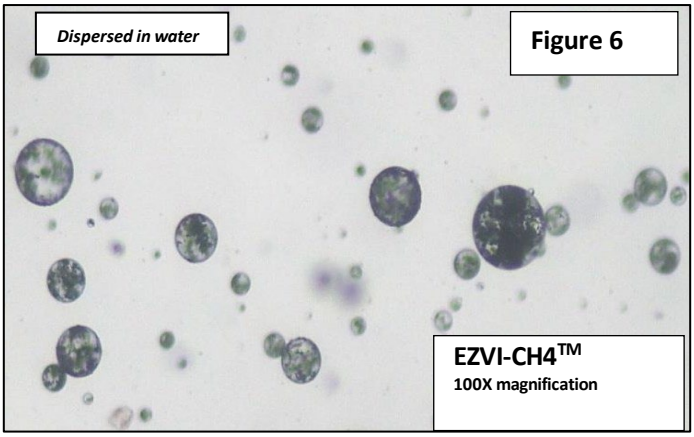
PROVECTUS' EZVI TECHNOLOGY ADVANCEMENTS

DNAPL Destruction with Controlled Methanogenesis - EZVI-CH4™

Chlorinated source areas typically have microbial populations that are inhibited by high dissolved contaminant concentrations (Brown *et al.,* 2009). When the EZVI technology is initially deployed the dissolved phase contaminant concentrations decrease dramatically and substantially (~ 90%) and enable the previously inhibited microbial communities to activate. Due to the ability of methanogens to multiply rapidly, they are typically the dominant hydrogenotrophs found in anaerobic biogeochemical conditions (Bates *et al.,* 2011). Due to the decrease in dissolved phase contaminant concentrations that occurs when utilizing the EZVI technology, combined with the ability of methanogens to rapidly multiply, it is common to see elevated methane production in conjunction with EZVI treatments.

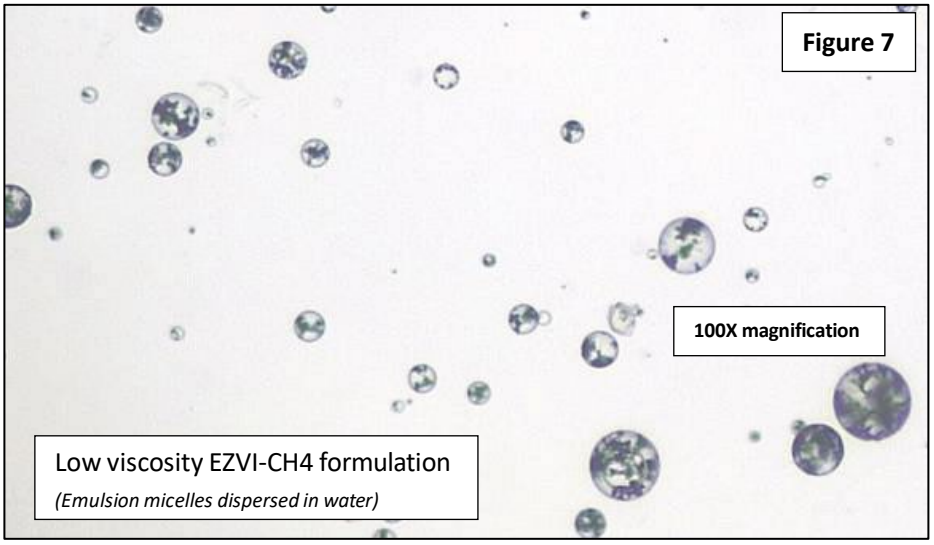
Therefore, Provectus' EZVI-CH4™ combines our patented antimethanogenic technologies (Provect-CH4™), with the EZVI technology to offer the only *in situ* DNAPL destruction technology with controlled methanogenesis. (**Figure 5** & **Figure 6**). The antimethanogenic chemistry is combined into the fermentable carbon component of the emulsion, so that methanogens are inhibited as the vegetable oil is fermented to organic acids. Multiple types of methane inhibitors are utilized, including RYR extract and select essential oils/saponins. A micrograph image of the EZVI-CH4™ product in water is depicted in **Figure 6**.





Decreased Viscosity Formulations

The NASA patented formulation for EZVI typically has a viscosity that ranges between 1,200 – 1,900 cP (Quinn *et al.,* 2005). This level of viscosity has been problematic during implementation dependent on soil conditions and the implementation method (e.g., injection equipment). To maximize subsurface distribution, and therefore contact with source materials, Provectus has developed a lower viscosity formulation of the EZVI technology that retains the correct emulsion structure and stability (**Figure 7**). This new formulation has a viscosity that ranges from 700 - 900 cP.



pH Stabilized and Catalyzed Formulations

The reaction kinetics of unamended ZVI with chlorinated solvents is pH dependent and inversely correlated (Chen *et al.,* 2001). As ZVI reacts with water, the surface of the ZVI is passivated by the deposition of iron oxides and oxyhydro-oxides (Liu *et al.,* 2006). Also, the pH of the water is increased due to the formation of hydroxyl ions. The increased pH conditions in turn enhances the rate of passivation of the iron surface due to formation of oxidized iron species. Additionally, the non-ionic surfactant used to manufacture the EZVI emulsion, is less stable with increasing pH conditions and could result in decreased emulsion stability under certain conditions in the aqueous phase of the emulsion (e.g., pH > 9.5).

Therefore, Provectus has formulated pH stabilized and catalyzed EZVI products which contain additives that will hydrolyze and provide acidity over time to the interior of the micelle. In addition, additives that will catalyze ZVI electron transfer processes, as well as act to directly reduce iron

oxides on the ZVI surfaces. These additives function to extend the duration of more optimal conditions for abiotic reductive dehalogenation reactions to occur and prevents the potential destabilization of the emulsion due to elevated pH conditions.

KEY FEATURES

- Emulsion Structure: Water drops dispersed within vegetable oil (water-in-oil)
- Viscosity: Low Vis formulation ~ 800 cP; standard formulations ~ 1,500 cP
- ZVI particle size = sub-micron to <5 micron
- Custom Formulations Available (ZVI: 5 to 20%; VO: 35-40%; AMR varies; weight basis)
- Shipping sizes (55 USG drums, 275 USG totes)
- Injection ready: Product is injection ready when received, does not require dilution

CONCLUSIONS

The NASA patented EZVI technology is an elegant and aggressive solution to the problem of in situ DNAPL destruction. However, the water-in-oil structure of the EZVI technology is critical for achieving direct DNAPL destruction via ISCR processes. Provectus EZVI products are not simply a mixture of emulsified vegetable oil (oil dispersed in water type emulsion) and ZVI. Rather, our EZVI products are the most advanced formulations of the NASA patented technology, and include:

- **CONTROLLED METHANOGENESIS** – EZVI-CH4™ is manufactured using Provectus' patented antimethanogenic reagents (AMR) technology incorporated into the fermentable component of the emulsion to inhibit excessive methanogenesis from occurring during initial fermentation of emulsion materials.
- **CATALYZED ZVI REACTIONS** – Our EZVI products can be provided with catalyzers to enhance and extend the reactivity of ZVI particles.
- **ENHANCED EMULSION STABILITY** – Our EZVI products can be provided with pH stabilization to maintain interior pH levels so that the emulsion structure has prolonged reactivity and stability in the subsurface.
- **LOWER VISCOSITY EMULSION** – Our EZVI products can be engineered, when appropriate, with decreased viscosity characteristics for enhanced installation (i.e., injectability).
- **CUSTOM EMULSION FORMULATION** – Our EZVI products are custom formulated for ZVI percentage, ZVI catalysis, AMR percentage, and viscosity, for each site. We will review your site information and work with you to develop a formula that is adapted for attaining your site-specific remediation goals.
- **EMULSION INTEGRITY** – Our EZVI products are manufactured per the NASA patent and quality checked during manufacturing to ensure emulsion structure is correct

REFERENCES

Arnold, W.A. and A. L. Roberts. (1998). Pathways and Kinetics of Chlorinated Ethylene and Chlorinate Acetylene Reaction with Fe(0) Particles. Environ. Sci. Technol. 1998. http://www.provectusenvironmental.com/marketing/zvi/Pathways_of_Chlorinated_Ethylene_EST 1998.pdf

Bates, S. T., Berg-Lyons, D., Caporaso, J., Walters, W., Knight, R., & Fierer, N. (2011). Examining the global distribution of dominant archaeal populations in soil. ISME Journal, 5, 908–917.

Brown, R.A., Mueller, J.G., Seech, A.G., Henderson, J.K. and Wilson, J.T. (2009) Interactions between biological and abiotic pathways in the reduction of chlorinated solvents. Remediation Journal 20(1), 9-20.

EPA. 2000. Engineered Approaches to In Situ Bioremediation of Chlorinated Solvents: Fundamentals and Field Applications. EPA 542-R-00-008.

Gillham, R.W. and S.F. O'Hannesin. (1994). Enhanced Degradation of Halogenated Aliphatics by Zero- Valent Iron. Ground Water, Vol 32., No. 6 pages 958 - 967. (http://www.provectusenvironmental.com/marketing/zvi/UW1994_Half-life_ZVI.pdf)

Kim, E-J., J-H Kim, Y-S-Chang, D. Ortega and P.G. Tratnyek. (2014) Effects of Metal Ions on the Reactivity and Corrosion Electrochemistry of Fe/FeS Nanoparticles. Environ. Sci. Technol. (http://www.provectusenvironmental.com/marketing/zvi/Tratnyek2014.pdf)

Liu, Y. and Lowry, G.V. (2006) Effect of particle age (Fe0 content) and solution pH on NZVI reactivity: H2 evolution and TCE dechlorination. Environ Sci Technol 40(19), 6085-6090.

O'Hara, S., Krug, T., Quinn, J., Clausen, C., and Geiger, C (2006) Field and Laboratory Evaluation of the Treatment of DNAPL Source Zones Using Emulsified Zero-Valent Iron. Remediation Journal March 2006.

O'Hara, S., Krug, T., Quinn, J., Clausen, C., and Geiger, C (2005) Field and Laboratory Evaluation of the Treatment of DNAPL Source Zones Using Emulsified Zero-Valent Iron. Presentation.

Quinn, J., Geiger, C., Clausen, C., Brooks, K., Coon, C., O'Hara, S., Krug, T., Major, D., Yoon, W.-S., Gavaskar, A. and Holdsworth, T. (2005) Field Demonstration of DNAPL Dehalogenation Using Emulsified Zero-Valent Iron. Environmental Science & Technology 39(5), 1309-1318.

Quinn, J., Clausen, C., Geiger, C., O'Hara, S., Krug, T., Watling, M., Ruiz, N., Su, C., Puls, R. (2009) Field Demonstration of DNAPL Dehalogenation Using Emulsified Zero-Valent Iron. Presentation

Reinhart, D., Clausen, C., Geiger, C., Quinn, J (2003) Zero-valent metal emulsion for reductive dehalogenation of DNAPLs. U.S. Patent 6,664,298 filed Oct. 2001 and issued Dec. 2003

Reinsch, B. C., B. Forsberg, R.L. Penn, C.S. Kim, and G. V. Lowry. (2010). Chemical transformations during aging of zero valent iron nanoparticles in the presence of common groundwater dissolved constituents. Environ. Sci. Technol. 2010, 44, 3455-3461

Su, C., Puls, R., Krug, T., Watling, M., O'Hara, S., Quinn, J. and Ruiz, N. (2017) Long-Term Performance Evaluation of Groundwater Chlorinated Solvents Remediation Using Nanoscale Emulsified Zerovalent Iron at a Superfund Site. In: Applying Nanotechnology for Environmental Sustainability DOI: 10.4018/978-1-5225-0585-3.ch005