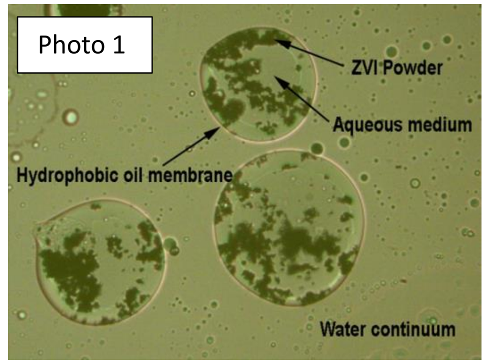
# EZVI-CH4™ Antimethanogenic ISCR DNAPL Technology

## TECHNOLOGY DESCRIPTION

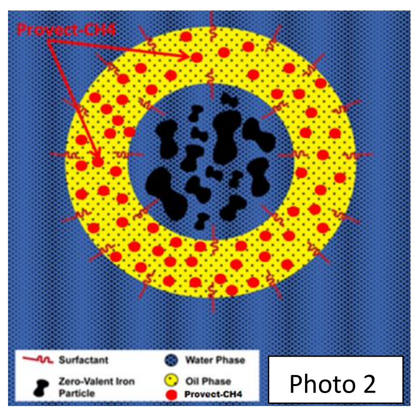



In 2003, scientists at the University of Central Florida (UCF) and the National Aeronautics and Space Administration's Kennedy Space Center (NASA-KSC) introduced Emulsified Zero-Valent Iron (EZVI) as a patented technology (Reinhart *et al.,* 2003) that combines food grade vegetable oil (VO) with a surfactant, elemental iron and water in a specific physical structure to enable direct DNAPL destruction utilizing a combination of abiotic and biotic processes (**Photograph 1**). Since then, millions of pounds of EZVI have been used at sites throughout the United States and in Canada and Australia.

In 2014, Provectus introduced Provect-CH4® which is a food-grade, natural source of Monacolin K (otherwise known as Lovastatin) and other statins used to prevent methane ($CH_4$) production by inhibiting the growth and proliferation of methanogenic Archaea (Scalzi *et al,* 2013, 2014). In environmental remediation applications, it can be used as a supplement to conventional enhanced reductive dehalogenation (ERD) and *in situ* chemical reduction (ISCR) amendments rendering them safer and more effective. These include:

- [Emulsified] Oils / Lecithins
- Sugars (lactate, dextrose, glucose)
- Other carbon sources (*e.g.,* molasses, whey)
- Plant based carbon (*e.g.,* cellulose and hemi-cellulose)
- Carbon + ZVI amendments (conventional ISCR reagents)

Antimethanogenic EZVI-CH4 uniquely combines the proven chemistry of NASA's EZVI Technology with the selective power of Provectus' Provect-CH4 methanogen inhibitors to yield a genuinely new, antimethanogenic DNAPL technology that is capable of direct *in situ* destruction of source materials (**Photograph 2**). It provides:




- Provect-CH4 methanogenic inhibitor (blended within fermentable H donor component of EZVI)
- Matching physical chemistry (hydrophobic) enables complete miscibility (contact) with DNAPLs
- Sequestration (phase partitioning) of hydrophobic contaminants (*e.g.,* halogenated hydrocarbons) into outer liquid oil membrane
- Mass flux reduction from source areas due to dramatic decrease in water solubility of contaminants
- Food grade soybean oil as a slow release, long term H donor
- Powdered, highly reactive, ZVI (< 5 $\mu$m size distribution) encapsulated within water/VO micelles (not in direct contact with ground water) will only react with contaminants that are hydrophobic
- Abiotic reactions primarily occur in the aqueous interior of emulsion where ZVI is suspended in water
- Biotic reactions primarily occur on the exterior of the emulsion and down gradient (hydrologically) of the EZVI implementation zone

## WHAT IS THE PROBLEM WITH METHANE?

There are recognized benefits to methanogens and of limited methanogenesis. For example, i) methanogens are known to play important roles in synergistic microbial ecology, ii) their metabolic activity can help maintain anoxic conditions in treatment zones (through seasonal changes), and iii) the activity of methane mono-oxygenases and other enzymes can stimulate co-metabolic activity of TCE/DCE/VC in redox-recovery zones. Hence, limited production of methane is part of a healthy ERD/ISCR application. However, excessive methane production can become dangerous and represents a costly waste of amendment.

Cost and Efficiency Issues: Production of methane is a direct indication that hydrogen generated from the electron donor amendments was used by methanogens instead of the target microbes (*e.g., Dehalococcoides* spp.), substantially reducing application efficiency. **Table 1** (below) presents a site example where hydrogen demand is calculated for a highly aerobic and oxidized source area measuring approximately 1,850 cubic yards. Hydrogen demand for complete dechlorination of all PCE and TCE mass to ethene within this source area example, including both adsorbed and dissolved contaminants, is less than the amendment consumed to generate 20 mg/L of methane. The same is true of reducing all dissolved oxygen, nitrate, sulfate, and bio-available iron and manganese competing electron acceptors within the hypothetical treatment zone. So, even though this example site is highly oxidized with relatively high total concentrations of PCE and TCE, generating just 20 mg/L of methane constitutes greater than 33% of the total amendment consumption based on moles of H2.

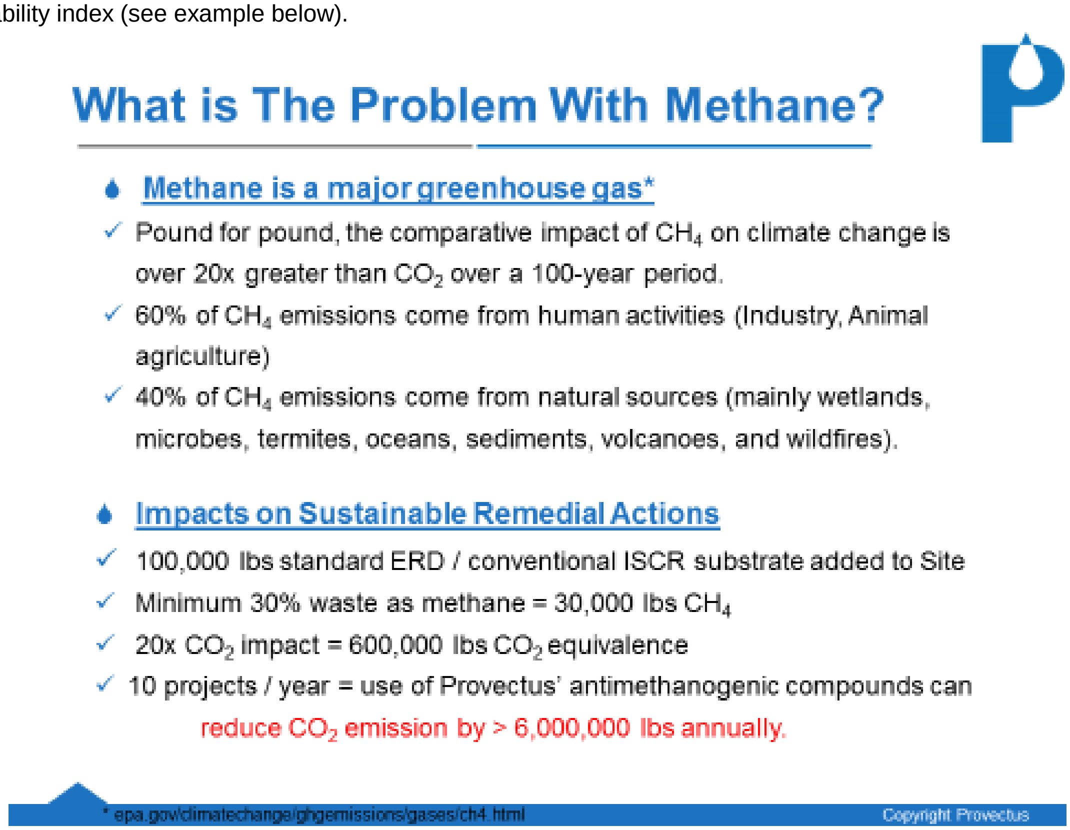
**Table 1: H Demand for Complete Dechlorination of PCE/TCE in Hypothetical Source Area.**

| Constituent | Groundwater Concentration (mg/L) | Molecular Weight (g/mol) | Moles of $H_2$ to Reduce Mole Analyte | Moles of $H_2$ Acceptor In Treatment Area |
|---|---|---|---|---|
| Contaminant Electron Acceptors (To End Product Ethene) | | | | |
| Tetrachloroethene (PCE) | 10.0 | 165.8 | 4 | 1,393 |
| Trichloroethene (TCE) | 7.0 | 131.4 | 3 | 364 |
| cis-1,2-Dichloroethene (cDCE) | 0.0 | 96.9 | 2 | 0 |
| Vinyl Chloride (VC) | 0.0 | 62.5 | 1 | 0 |
| Complete Dechlorination (Soil+Groundwater) Subtotal | | | | **1,757** |
| Native Electron Acceptors | | | | |
| Dissolved Oxygen | 9.0 | 32 | 2 | 199 |
| Nitrate (as Nitrogen) | 9.0 | 62 | 3 | 682 |
| Sulfate | 50.0 | 96.1 | 4 | 736 |
| $Fe^{+2}$ Formation from $Fe^{+3}$ | 20.0 | 55.8 | 0.5 | 63 |
| $Mn^{+2}$ Formation from $Mn^{+4}$ | 10.0 | 54.9 | 1 | 64 |
| Baseline Geochemistry Subtotal | | | | **1,745** |
| Hydrogen Waste for Methane Formation | | | | |
| Methane Formed | 20.0 | 16 | 4 | **1,769** |
| ***Initial Treatment Area Hydrogen Usage*** | | | | **5,271** |

Potential Health and Safety Issues: Methane is considered to be a major greenhouse gas. It is explosive, with an LEL of 5% and an UEL of 15%. As a result of the microbial fermentation process, methane will be produced in most situations following the addition of any conventional ERD or ISCR amendment. Excessive and extended production of methane can result in elevated in groundwater concentrations (as high as 1,000 ppm have been reported) which can lead to accumulation in soil gas subsequently impacting indoor air. While this is perhaps more relevant in urban settings where methane can accumulate in basements, under slabs/foundations and/or migrate along utility corridors, excessive methane production has also been observed in more rural settings and other open spaces.

New and Emerging Regulatory Issues: State specific regulations for methane in groundwater have been promulgated, with others pending for soil gas and indoor air. For example, current regulations for methane in groundwater vary from *ca*. 10 to 28 mg $CH_4$/L (Indiana Department of Environmental Management, 2014). Notably, several ERD projects which intended to use liquid carbon (emulsified oils) sources have failed to receive regulatory approval due to issues associated with excessive production of methane during previous technology applications (Personal Communication - States of California, Indiana, Florida, Michigan, Minnesota, North Carolina). As a result, many remedial practitioners proactively design contingencies for conventional ERD/ISCR implementation in the event that methane exceeds a threshold level ranging from 1 to 10 ppm groundwater. These contingencies often entail expensive and extensive systems for treating methane in soil gas/vapor captured via SVE systems.

Sustainability Issues: Uncontrolled methanogenesis can be interpreted (by some) to represent an avoidable contribution to greenhouse gas emissions hence its active control can have a positive impact on one's overall sustainability index (see example below).



## EZVI-CH4™ PRIMARY FEATURES

EZVI-CH4 is the only technology engineered to directly destroy DNAPL while significantly decreasing the wasteful consumption of hydrogen donor by actively controlling the production of methane. The benefits of the combined technologies are notable:

- More Cost Efficient: By inhibiting the growth and proliferation of methane producing Archaea, at least a 30% increase in hydrogen available for dissolved phase biotic dehalogenation processes will be realized.
- More Effective: EZVI-CH4 is fully miscible (due to hydrophobic nature) with DNAPL source materials. This miscibility provides significant improvement in contacting, and therefore destroying, organic contaminants. The ZVI utilized in EZVI-CH4 is protected within a micellular structure that only enables it to react with contaminants that have hydrophobic properties.
- Safer: Methane is explosive with an LEL of 5% and an UEL of 15%. Production of methane will result from the addition of any conventional ERD or ISCR amendment: excessive and extended production of methane can result in elevated in groundwater concentrations (>100 ppm have been reported) which can lead to accumulation in soil gas subsequently impacting indoor air. State specific guidelines for methane in groundwater have been published, with others pending for soil gas and indoor air.
- Reduced Potential for Air Exceedances: Excessive methane production can desorb contaminants from the DNAPL and induce their migration from the source area. This can be especially problematic immediately after the remedial construction phase.
- Green and Sustainable Technology: Formulated using renewable resources (plant extracts), utilizes natural processes for contaminant destruction; can significantly reduce carbon footprint of remediation projects by decreasing O&M activities associated with the operation of P&T systems for hydraulic control of source contamination.
- Patented Technologies: Technology end users and their clients are fully protected from all Patent and other legal issues.
- Ease of Use:
  - Product is injected directly into delineated source areas
  - Custom emulsion formulations available to address unique situations
  - Product is delivered to the site in an injection ready state
  - No laborious material transfers and dilutions
  - EZVI-CH4 formulation is site specific
  - Successfully implemented in wide range of soil types (*e.g.* clays, sands, saprolites, fractured bedrock)
  - Avoids cost and need for contingency planning to manage excessive methane production associated with ISCR/ERD remedial approaches (SVE/AS off gas treatment)
- Longevity (> 3 years): EZVI has been shown to be effective in providing source material destruction and enhanced biological reactions for periods exceeding 4 years during field applications.
- Mass Flux Reduction: The lipophilic nature of the VO component of the EZVI emulsion acts as a co-solvent for the DNAPL to phase partition into, thereby dramatically lowering the water solubility of the DNAPL materials and providing significant **MASS FLUX REDUCTION** from source areas (typically > 90% reduction in source area dissolved phase concentrations within < 6 months).
- Cost Competitive: At a list price of $2.75/lb, or $24.60/USG (volume discounts will apply) for EZVI-CH4 containing 38% (weight) carbon + 10% (weight) micron ZVI + 2% to 4% (weight) methane inhibitor, this is the most cost efficient way of procuring these technologies. When all factors are considered EZVI-CH4 is an excellent value that will greatly benefit your customers.

## APPLICATION GUIDELINES:

Using our combined experiences from the past 25 years successfully applying ISCR (both biological and abiotic) at hundreds of sites throughout the world, we developed an application range that incorporates site specific analytical data as well as knowledge of successful application rates from similar sites under similar conditions. Typically, our successful application dose ranges from *ca*. 1 to 2 lbs. of amendment per cubic foot of aquifer for injections (10% - 15% assuming 20% porosity), dependent on DNAPL/source material conditions (*e.g.,* sorbed vs free phase). The amount of EZVI-CH4 required to destroy DNAPL contaminants for a specific source area can be determined as follows:

- Targeting injection within groundwater isoconcentration lines equal to or greater than 10% of the water solubility of the parent compound (*e.g.* for TCE ≥ ~ 120 ppm);
- Once we have the soil volume associated with the above isoconcentration limit at a site, we typically target approximately 10 - 15% of the effective porosity with the EZVI technology at sites with permeable soils (*e.g*. sands/silts);
- For sites with tighter soils we work directly with the implementer to understand their implementation process and we determine EZVI volume based on the site-specific implementation process;
- The Provect-CH4 component of EZVI-CH4 is suspended within the hydrogen donor (liquid oil membrane) of the emulsification, thereby providing sustained methane inhibition throughout the fermentation of this material.
- Viscosity = 1,100 cP at 20º C
- Specific Gravity = 1.05 – 1.10 g/cc

## ORDERING

**CONTACT US FOR A COMPLIMENTARY SITE EVALUATION**

**PROVECTUS ENVIRONMENTAL PRODUCTS, INC.**

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