



Dispelling Myths and Extolling the Virtues of the EZVI Technology

Session D6: Advances in Amendment Formulation
Wednesday May 24, 2017

Greg Booth, Jim Mueller, – Provectus Environmental Products, Inc.
greg.booth@provectusenv.com

Mike Scalzi, Wade Meese –
Innovative Environmental Technologies, Inc. (IET)

Cherie Yestrebsky, Chris Clausen (ret.) –
University of Central Florida (UCF)



6/6/2017

4th International Conference on Bioremediation and
Sustainable Environmental Technologies
May 22-25, 2017
Miami, FL

Presentation Outline



- 💧 **Background and History**
- 💧 **Technology Description**
- 💧 **Implementation**
- 💧 **Technology Update**
- 💧 **Cost & Benefits**
- 💧 **Summary**

Presentation GOAL:

For you to gain a good understanding of what the EZVI technology is (and isn't), when it is an appropriate remedial alternative and what are the most recent advancements to the technology.

Background



History – DNAPL Remediation Issues

- **Physical Chemistry**

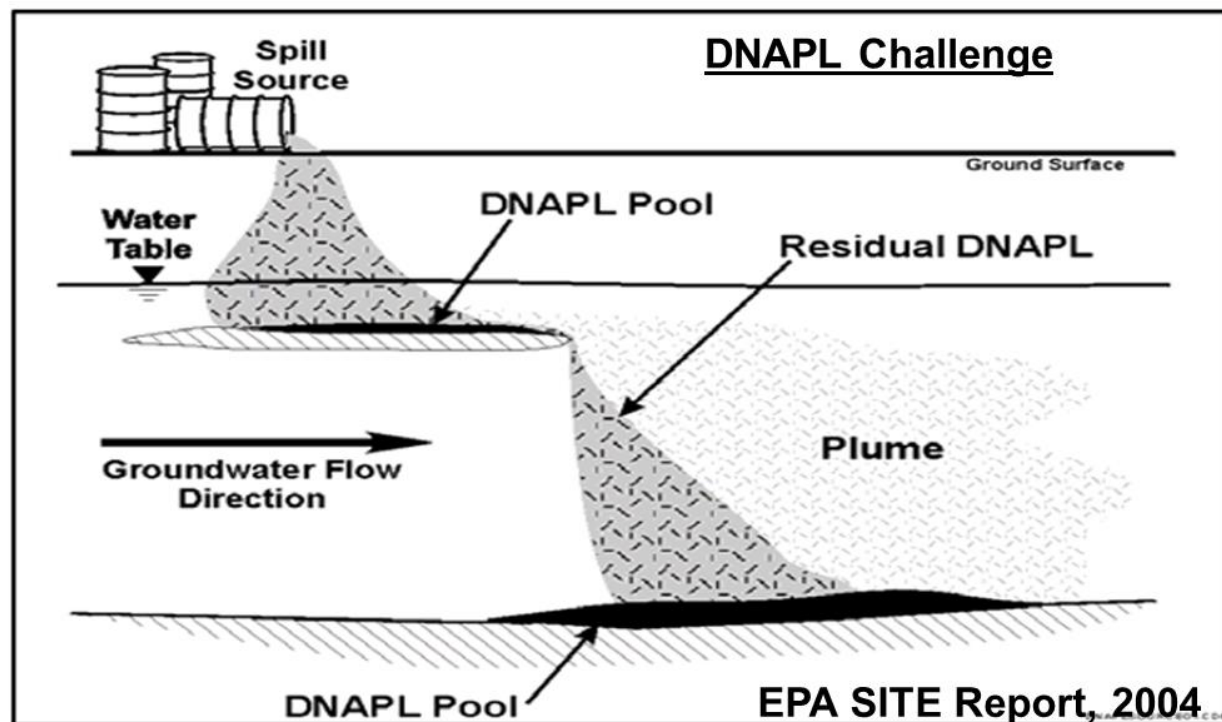
- Hydrophobic
- Dense & low viscosity
- Low water solubility

- **Location**

- Precision

- **Treatment**

- Contact



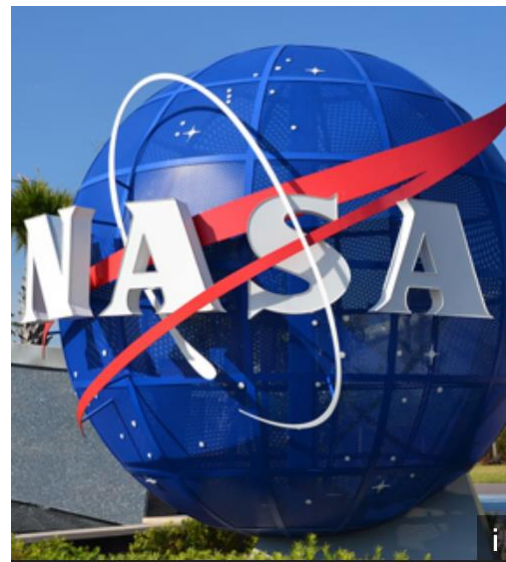
Background



History – Invention of EZVI

Scientists at UCF and NASA (KSC) invented EZVI to address CHC DNAPL contamination at the Kennedy Space Center in Cape Canaveral, FL.

NASA utilized TCE as a degreaser for rocket engine parts throughout the 1960's.



Background & History



DEVELOPMENTS TO DATE

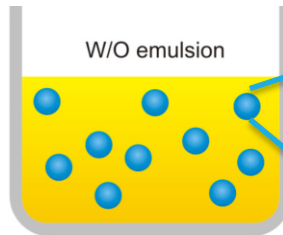
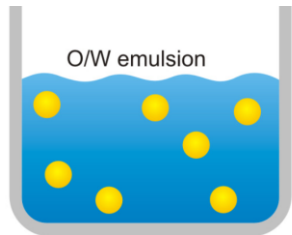
- 1997 – 1998: Conceptualization/Development
- 1999 – 2002: Proof of Concept R&D at UCF/KSC
- 2003 – 2004: Pilot studies – EPA SITE Evaluation
- **2005 – 1st FULL SCALE implementation – PAFB**
- 2005 – Present: Various Applications across USA, Canada, EU
- 2015 – Technology Enhancement – new product **EZVI-CH4™**
- 2015 – Present: Continued Optimization of the EZVI product

Technology Description



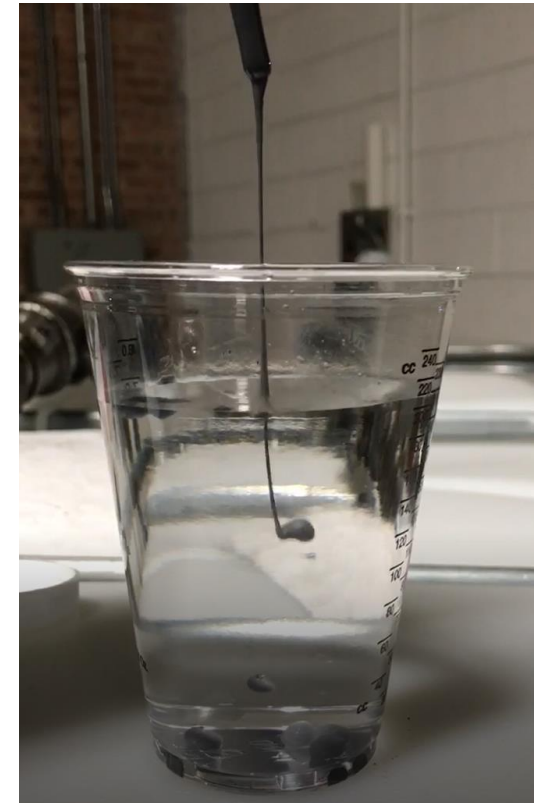
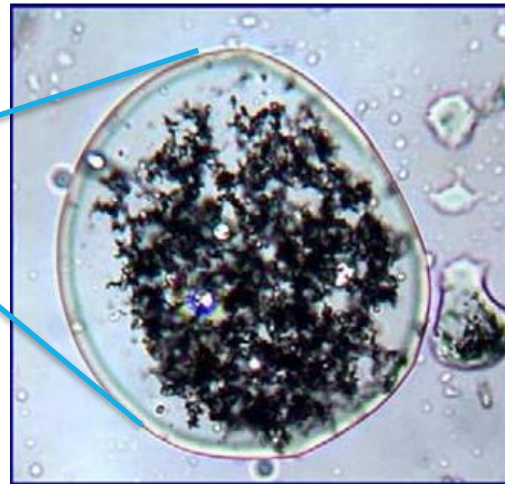
What is EZVI?

- Surfactant stabilized, water-in-oil emulsification with small micron ($< 5 \mu\text{m}$) ZVI particles suspended in the water drops.
- EZVI is a DNAPL (hydrophobic, sinker)



● Oil

● Water



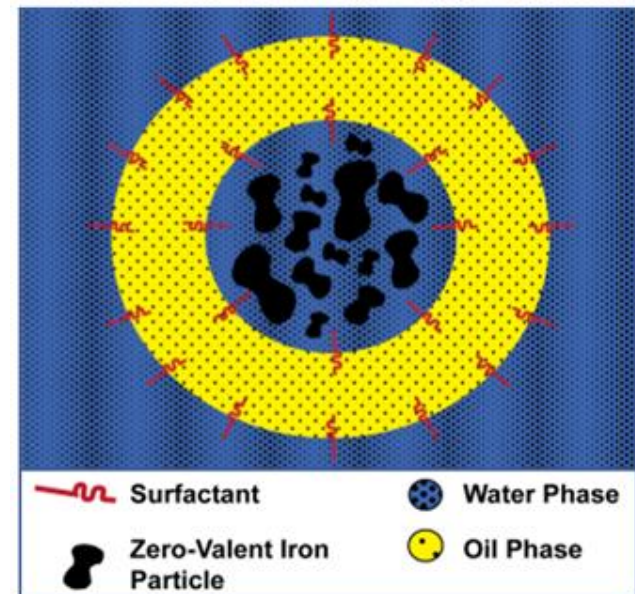
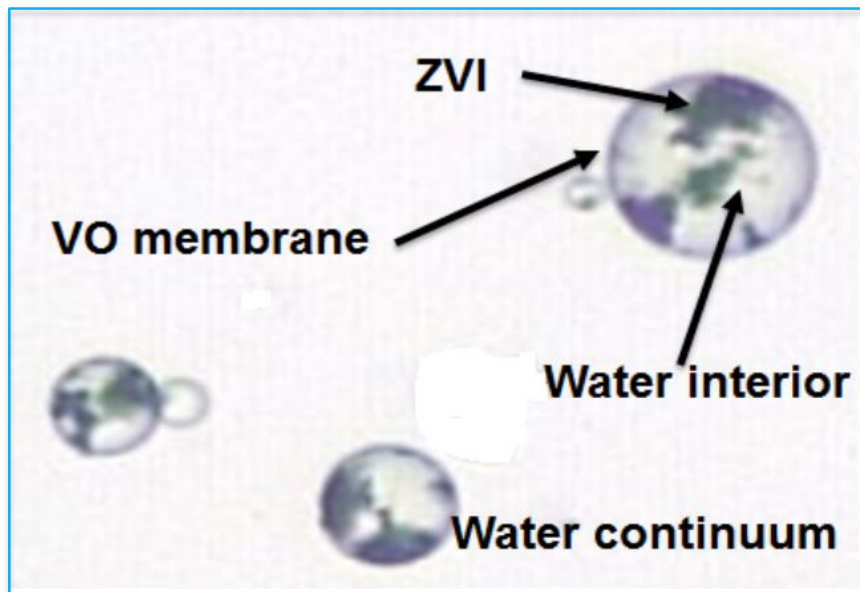
Technology Description



How does it work? -

- Sequestration
- Dissolution
- Reductive dehalogenation (abiotic & biotic)

Emulsion Structure is KEY

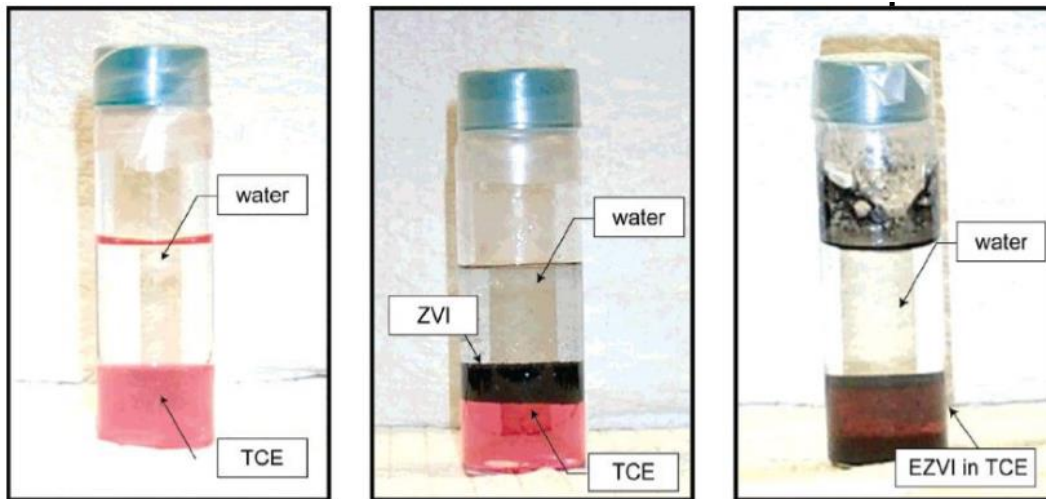


Technology Description



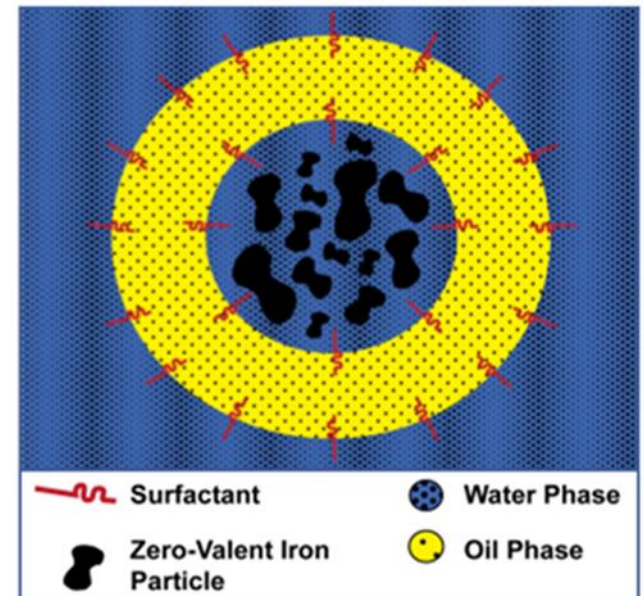
What is the innovation?

- **Miscibility** with DNAPLs
- **Combination Technology** utilizing abiotic & biotic processes AND physical chemistry
- Emulsion **structure** is key



Miscible with DNAPL

Ref: Brooks et al., 2000



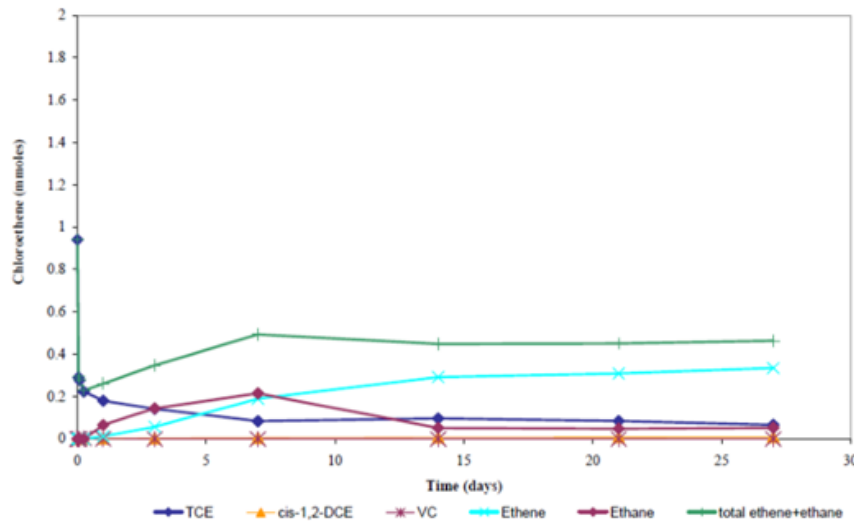
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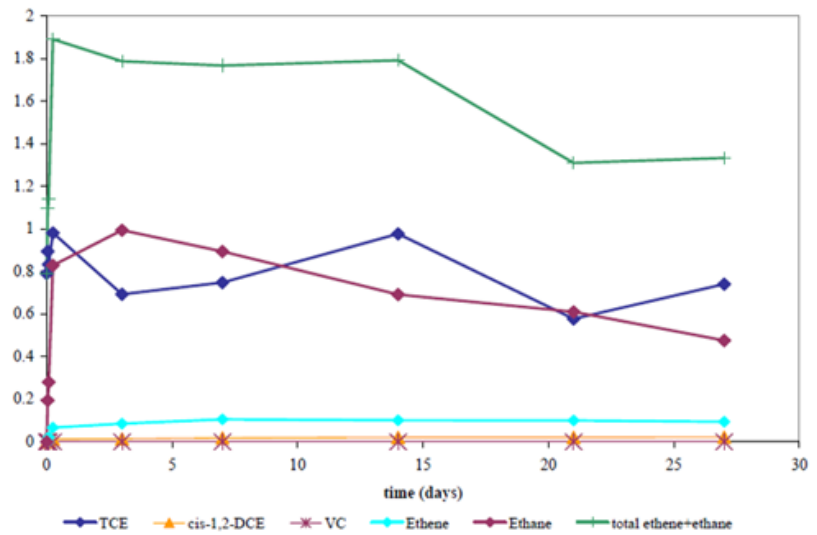
How is EZVI Unique?

EZVI vs ZVI

- Due to sequestration step EZVI provides reduced Mass Flux
- Emulsion structure is key



EZVI and KB-1 DNAPL



ZVI and KB-1 DNAPL

Ref: O'Hara et al., 2005

Implementation



- Engineered as an *in situ* source area destruction technology
- Emplaced directly into source area soils
- Effective in VADOSE and SATURATED soils
- EZVI delivered via:
 - Pneumatic Enhanced IDS
 - Hydraulic & Pneumatic Fracturing
 - Soil Mixing



Implementation



When is EZVI an option?

- DNAPL is present:
 - Parent compound(s) in GW \geq 10% of water solubility
 - The site is conducive to a reductive, *in situ* approach

How much do I need?

- Dosing is based on soil pore volume (not stoichiometry)
- Typical approach utilizes ~ 10% of available pore space

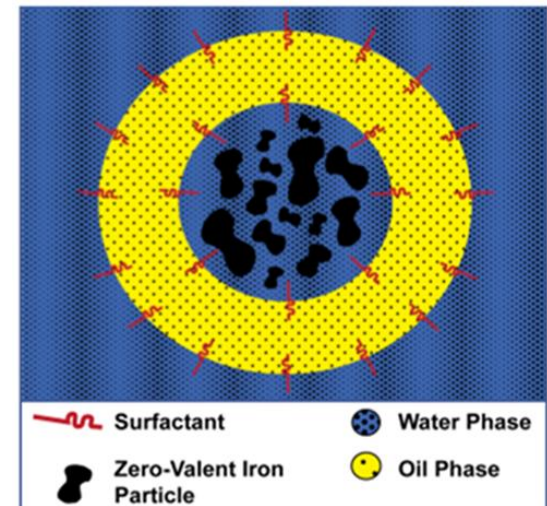
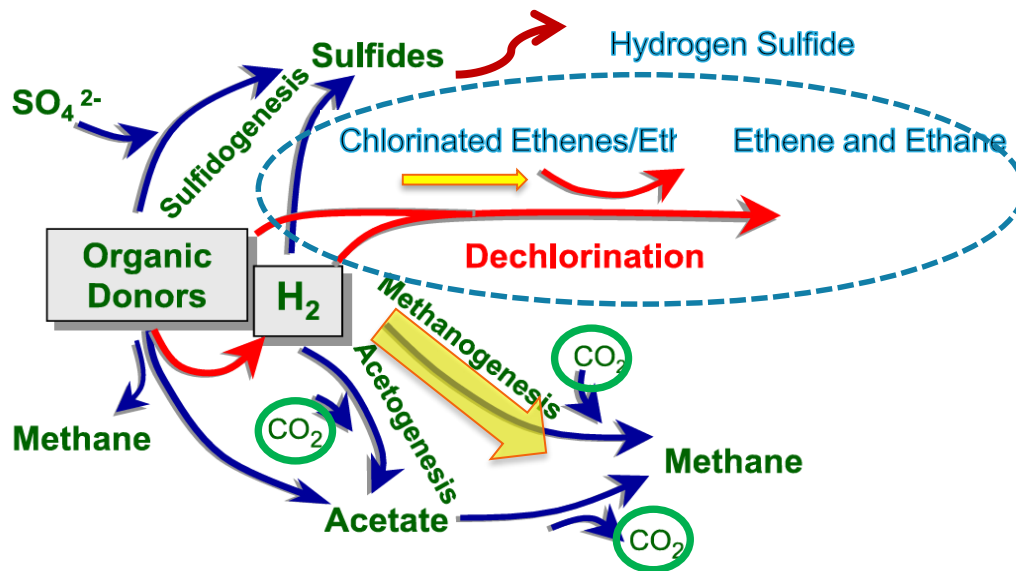
Is there a standard formulation?

- Custom formulation is available
- Typical formula contains 10% ZVI (wt.%)

Technology Update – Hydrogen is the Currency

Where Does it Go? = Cost and Efficiency Issues: Methanogens dominate anaerobic ecosystems and they can hinder dechlorination by competing for H_2 with dechlorinating bacteria (Yang and McCarty, 1998; yellow arrows modified by Proventus).

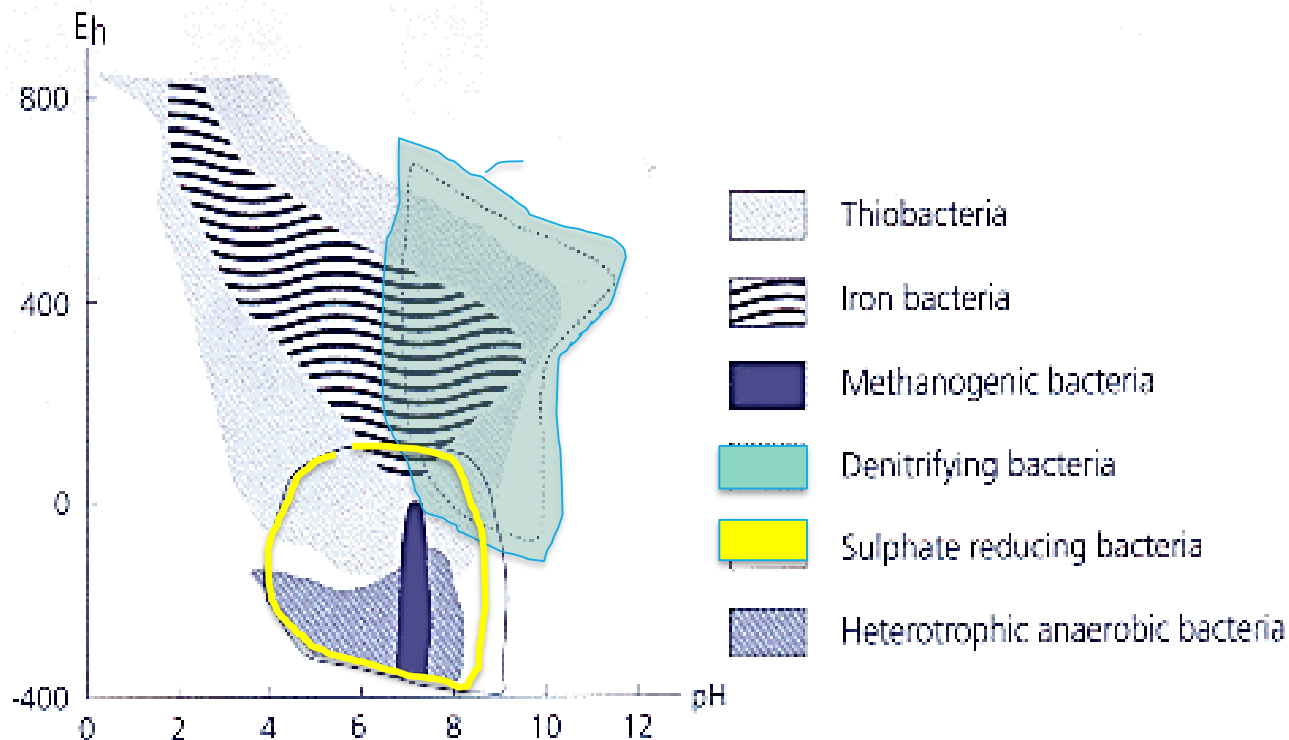
Optimizing Biological Processes



Technology Update – Idealized Eh pH Ranges for Microbial Growth



Microbe	Doubling Times
Dehalococcoides spp.	24 to 48 hours
Methanogens with cytochromes	10 hours
Methanogens without cytochromes	1 hour



Technology Update — What is The Problem With Methanogens?



- 💧 **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.

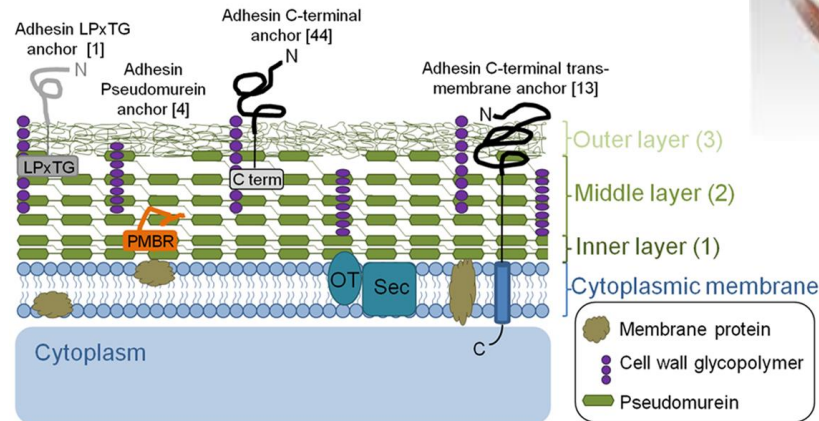
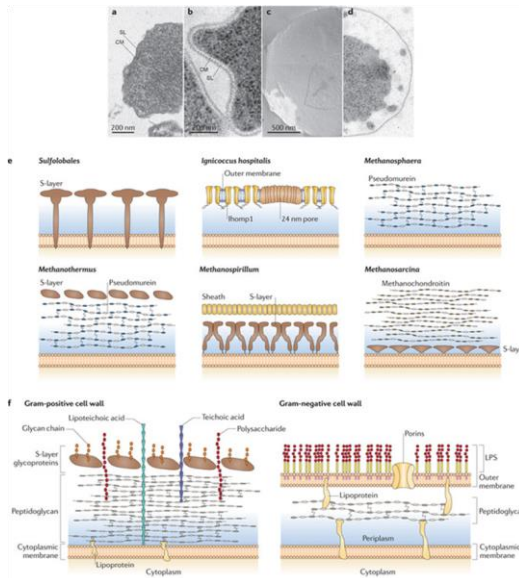
Constituent	Groundwater Concentration (mg/L)	Molecular Weight (g/mol)	Moles of H ₂ to Reduce Mole Analyte	Moles of H ₂ Acceptor In Treatment Area
Contaminant Electron Acceptors (To End Product Ethene)				
Tetrachloroethene (PCE)	10.0	165.8	4	1,393
Trichloroethene (TCE)	7.0	131.4	3	364
cis-1,2-Dichloroethene (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

Even in a highly oxidized setting 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.

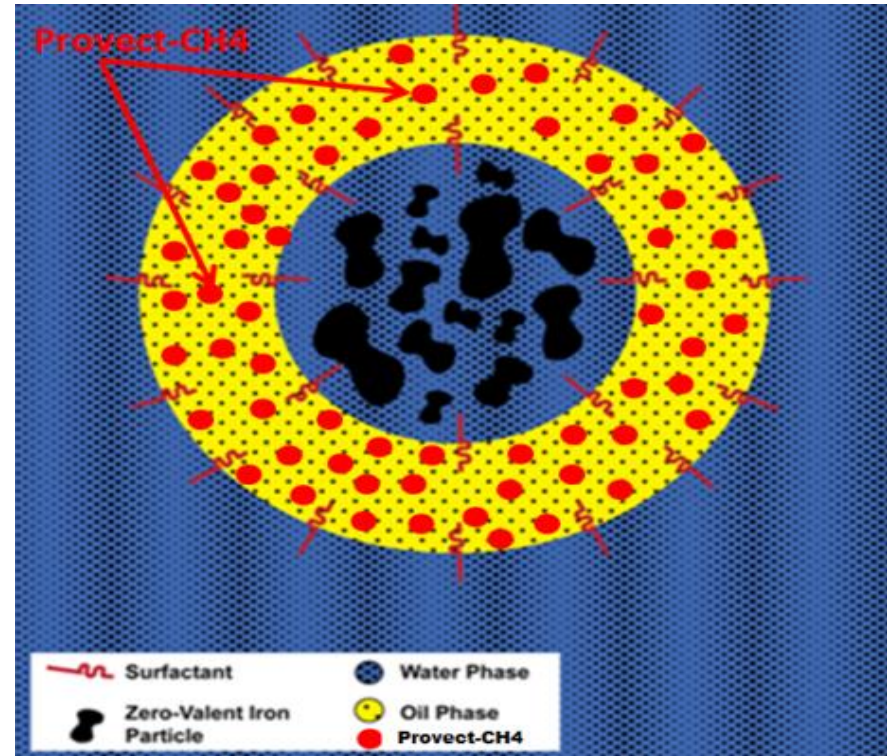
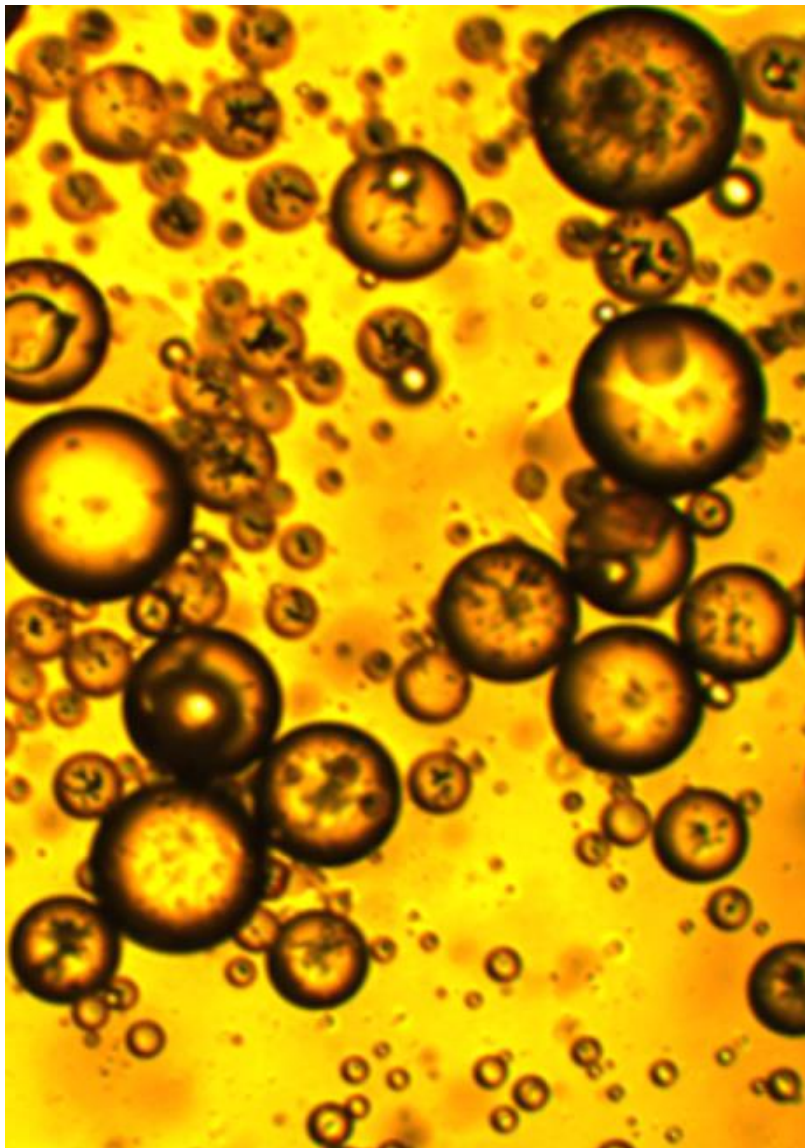
Technology Update – How Do We Control Methanogens?



- Methanogens are genetically unique – **Archaea**
- Utilizing naturally occurring statins (RYS Extract) and select essential oils/saponins to disrupt enzyme and coenzyme processes unique to methanogens



Technology Update - EZVI-CH4™ Reduced Methane *in situ* DNAPL Remediation Technology



New product - **EZVI-CH4™**

Research & Development

Enhancing Product Implementability

EZVI Viscosity:

- Can be an issue for subsurface injections:
 - NASA patented formulation = $\sim 1,200 - 1,900$ cP
 - Provectus' low viscosity formulation = ~ 800 cP
 - R&D into viscosity adjustment is ongoing



Research & Development

Optimizing Abiotic Processes

Reactivity:

- Enhance the reactivity of the micelle interior
 - ZVI surface passivation
 - Electron transfer processes

Emulsion Stability:

- Manage interior pH levels to prevent destabilization of emulsion and minimize deposition of iron oxides



Cost & Benefit



Cost

- Varies based on product formulation and soil pore volume

Benefits

- Directly destroys halogenated contaminant source (DNAPL)
- Controlled methanogenesis with **EZVI-CH₄TM**
- Effective in VADOSE soils
- Combination technology utilizes abiotic & biotic processes
- Utilizes contaminant physical chemistry to provide **significant reduction in source area MASS FLUX**

Summary



Newest Advancements to the EZVI technology:

- **EZVI-CH4™:** *In-situ* DNAPL destruction with controlled methanogenesis and lower viscosity (~ 800 cP).
- **Upcoming Advancements:** Ongoing R&D includes optimization of chemistry on the interior of the emulsion to include pH stabilization and enhanced reactivity to expand the scope of treatable contaminants.

Critical Innovation for NASA Patented EZVI Technology:

- The **STRUCTURE (water-in-oil type)** of the EZVI emulsion is key for the technology to perform as patented. EZVI is **NOT** simply a mixture of emulsified vegetable oil (oil dispersed in water type emulsion) and ZVI.

Stop By Our Booth!



BOOTH 224: Provectus Environmental Products, Inc.

