Dispelling Myths and Extolling the Virtues of the EZVI Technology

Session D6: Advances in Amendment Formulation
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Presentation Outline

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

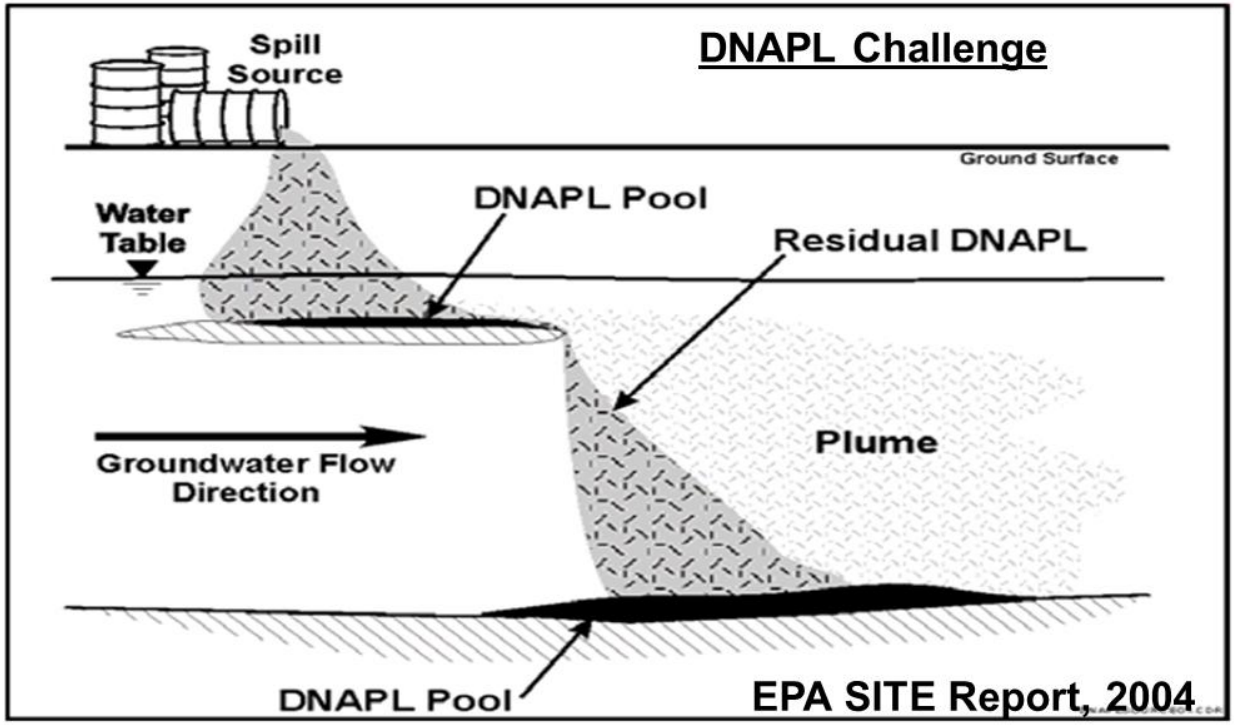
Presentation GOAL:

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

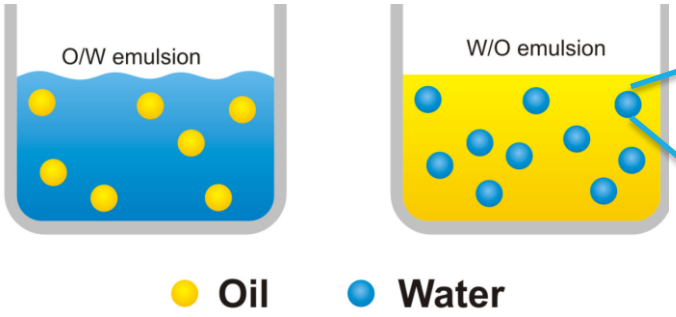
- 1997 – 1998: Conceptualization/Development
- 1999 – 2002: Proof of Concept R&D at UCF/KSC
- 2003 – 2004: Pilot studies – EPA SITE Evaluation
- **2005 – 1st FULL SCALE implementation – PAFB**
- 2005 – Present: Various Applications across USA, Canada, EU
- 2015 – Technology Enhancement – new product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

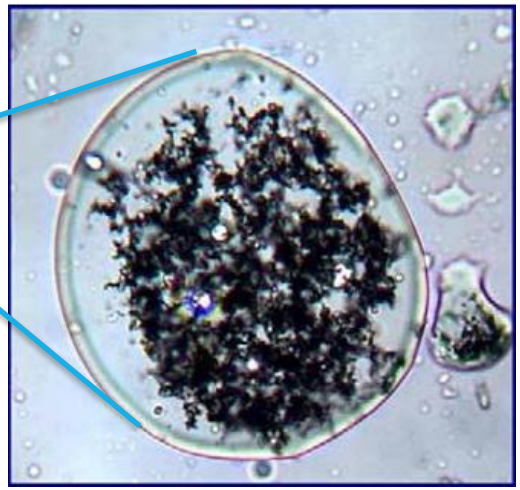
Technology Description

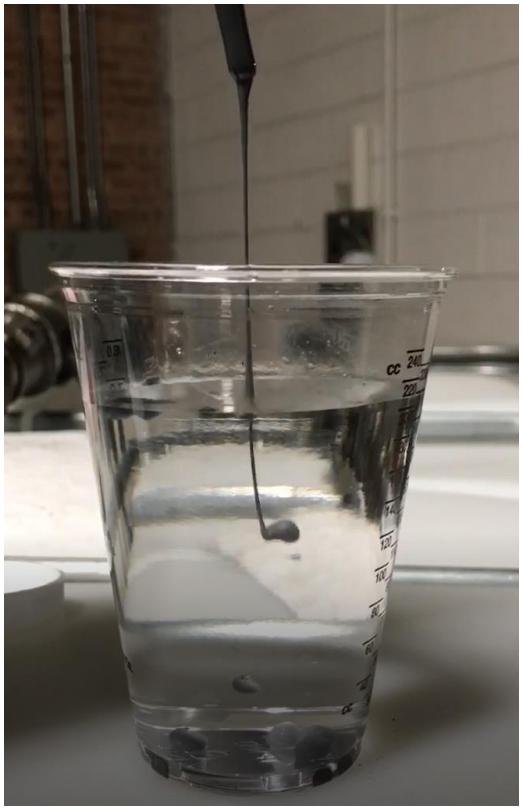
What is EZVI?

- Surfactant stabilized, water-in-oil emulsification with small micron (< 5 μm) ZVI particles suspended in the water drops.

- EZVI is a DNAPL (hydrophobic, sinker)





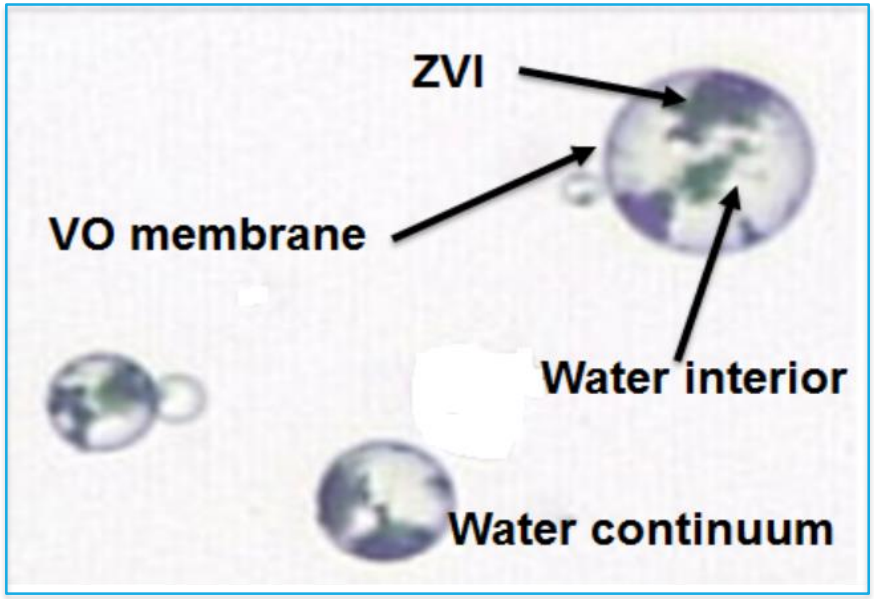


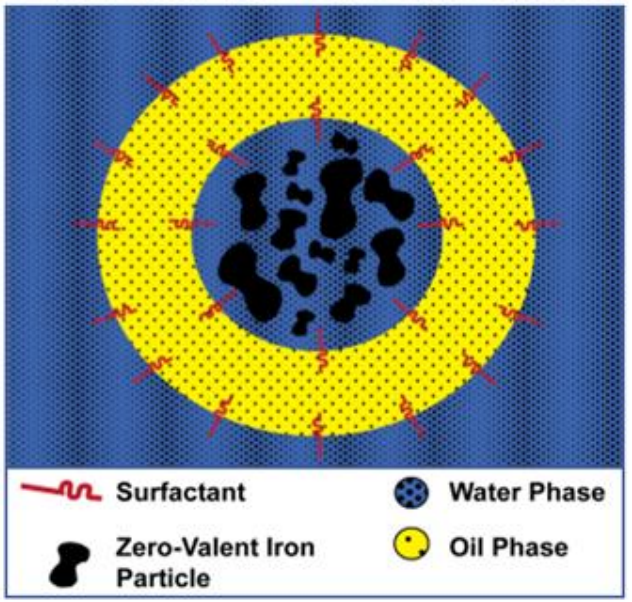
Technology Description

How does it work? -

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

Emulsion **<u>Structure is KEY</u>**

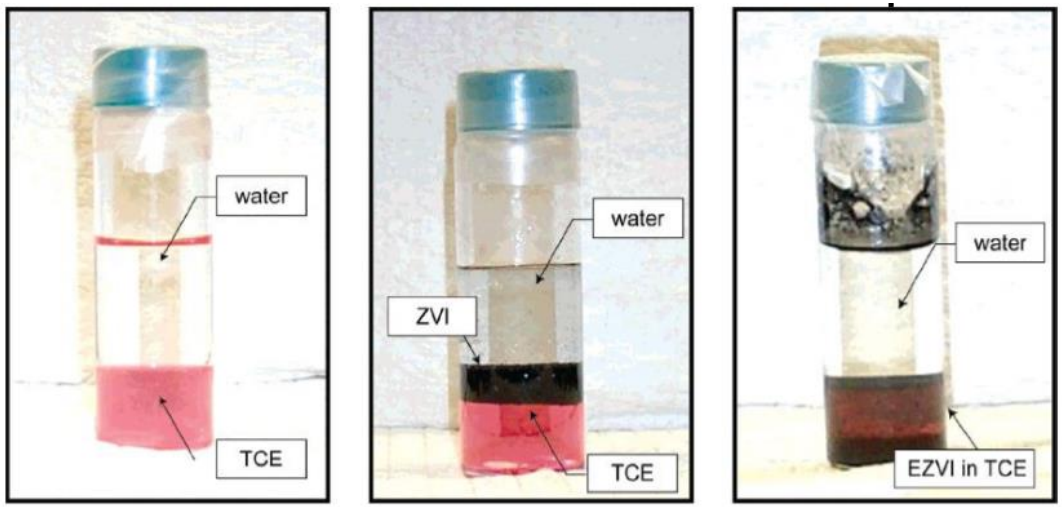




Technology Description

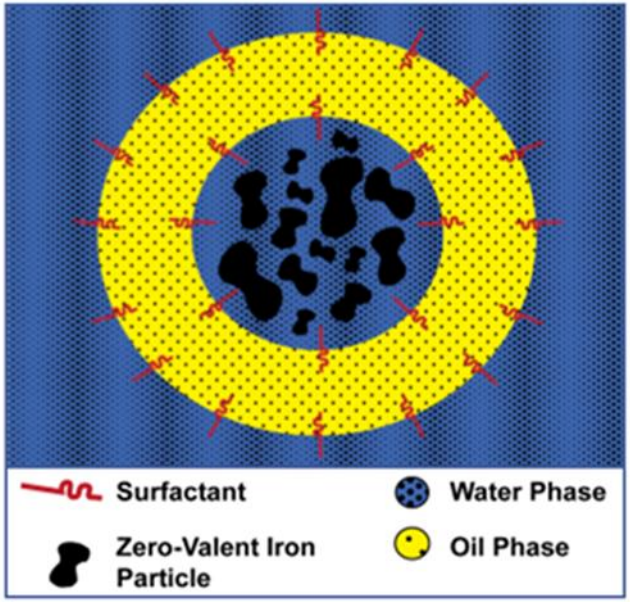
What is the innovation?

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



Miscible with DNAPL

Ref: Brooks et al., 2000

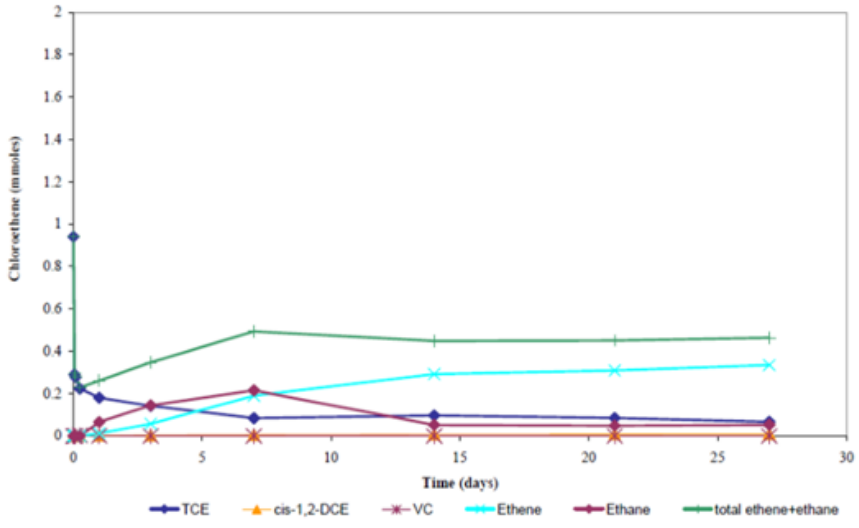


Technology Description

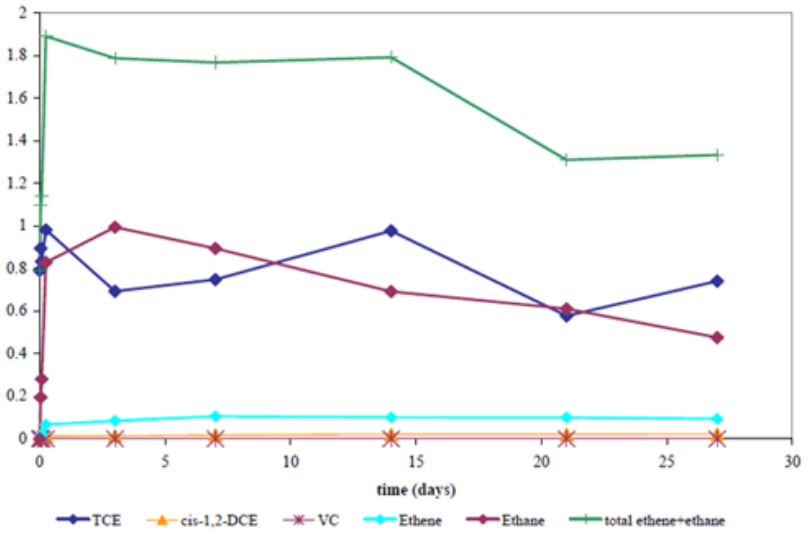
How is EZVI Unique?

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 ≥ 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

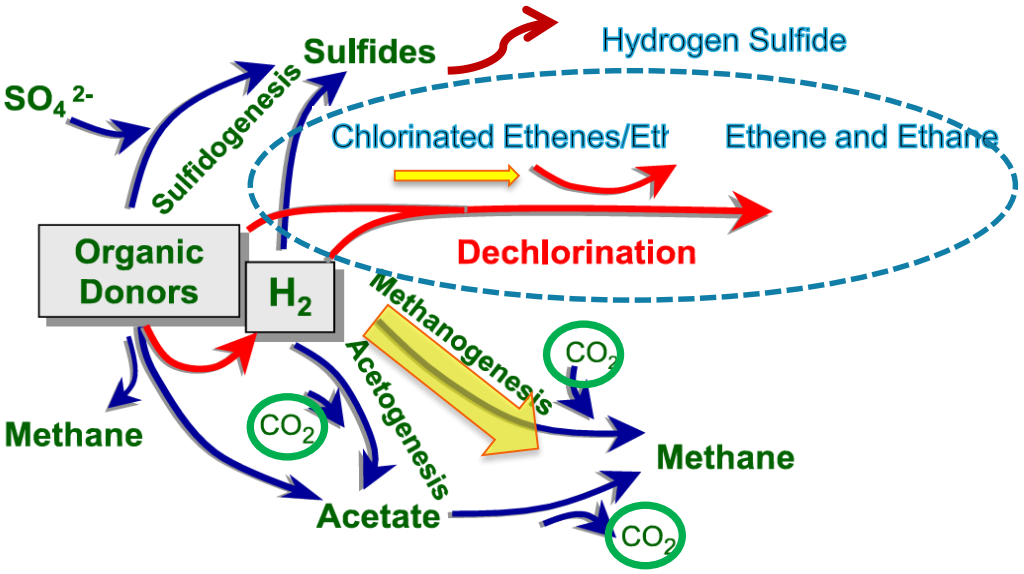
Is there a standard formulation?

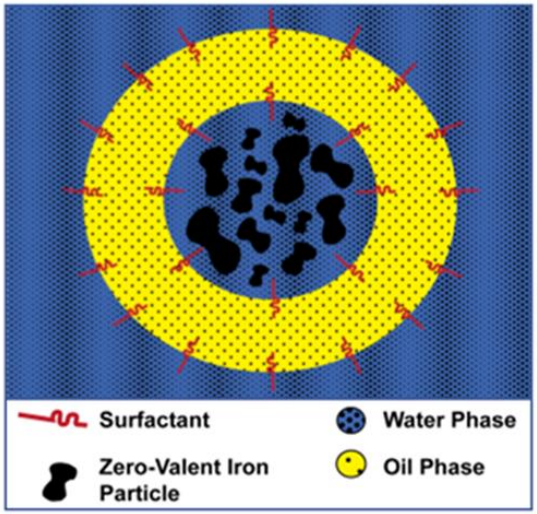
- Custom formulation is available
- Typical formula contains 10% ZVI (wt.%)

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 Provectus).

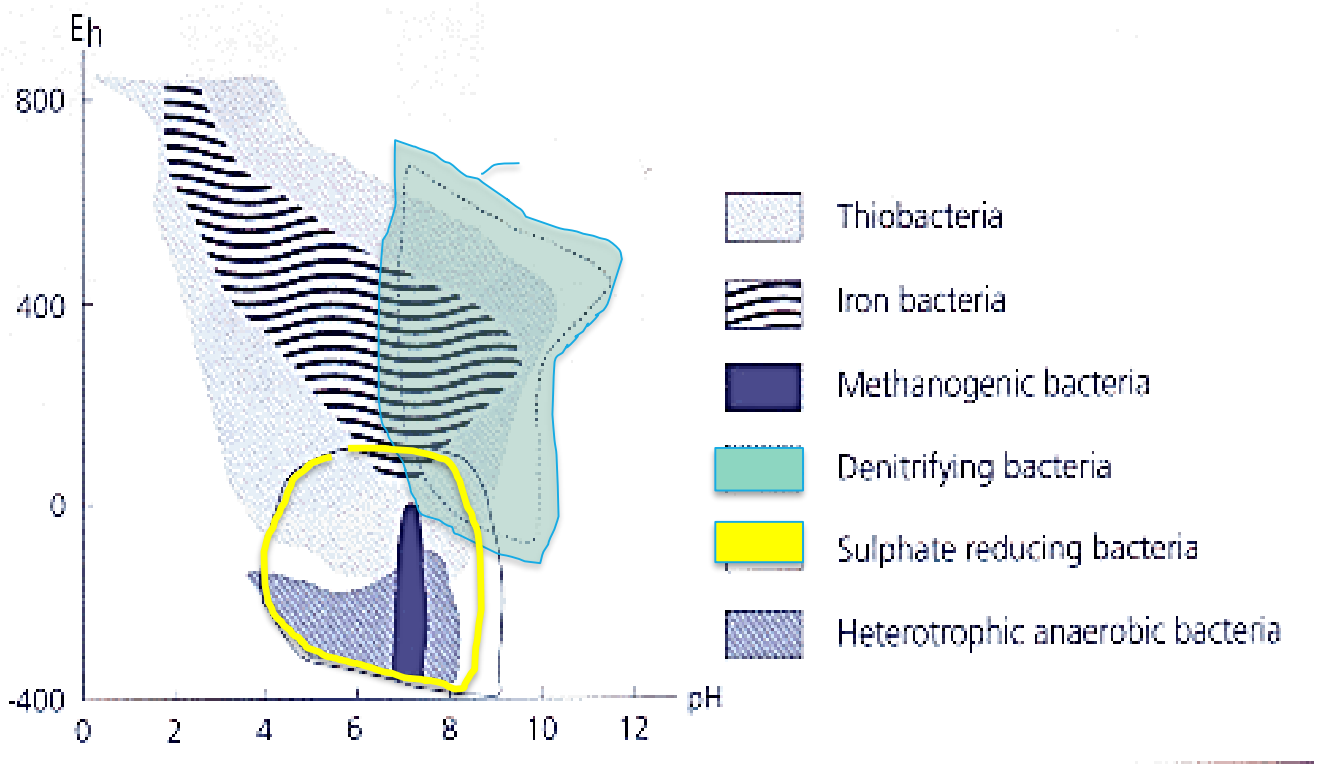
Optimizing Biological Processes





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



Zajic, 1969. Sigma Aldrich

Technology Update – What is The Problem With Methanogens?

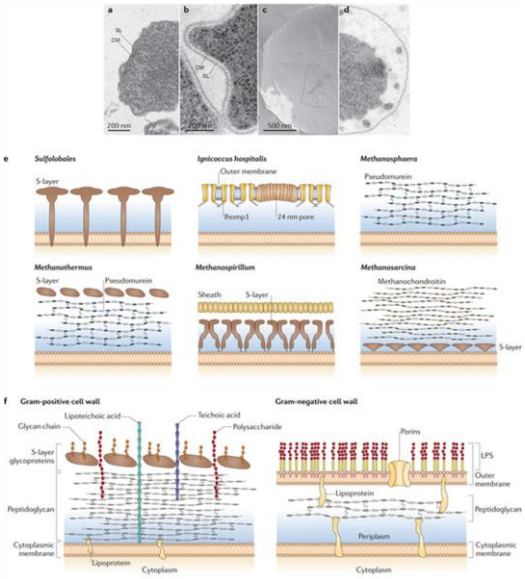
- **Cost and Efficiency Issues**: Production of methane is a direct indication that hydrogen generated from the electron donor amendments was used by methanogens instead of the target microbes (*e.g., Dehalococcoides spp.*), substantially reducing application efficiency.

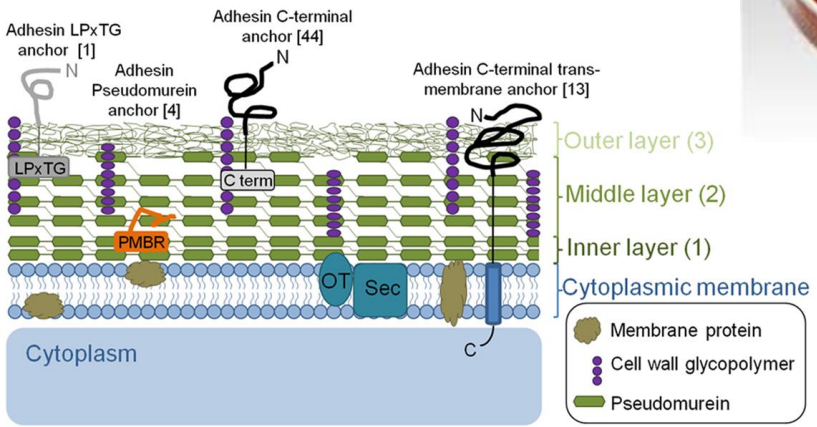
Constituent	Groundwater Concentration (mg/L)	Molecular Weight (g/mol)	Moles of H_2 to Reduce Mole Analyte	Moles of H_2 Acceptor In Treatment Area
Contaminant Electron Acceptors (To End Product Ethene)				
Tetrachloroethene (PCE)	10.0	165.8	4	1,393
Trichloroethene (TCE)	7.0	131.4	3	364
cis-1,2-Dichloroethene (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 H_2.

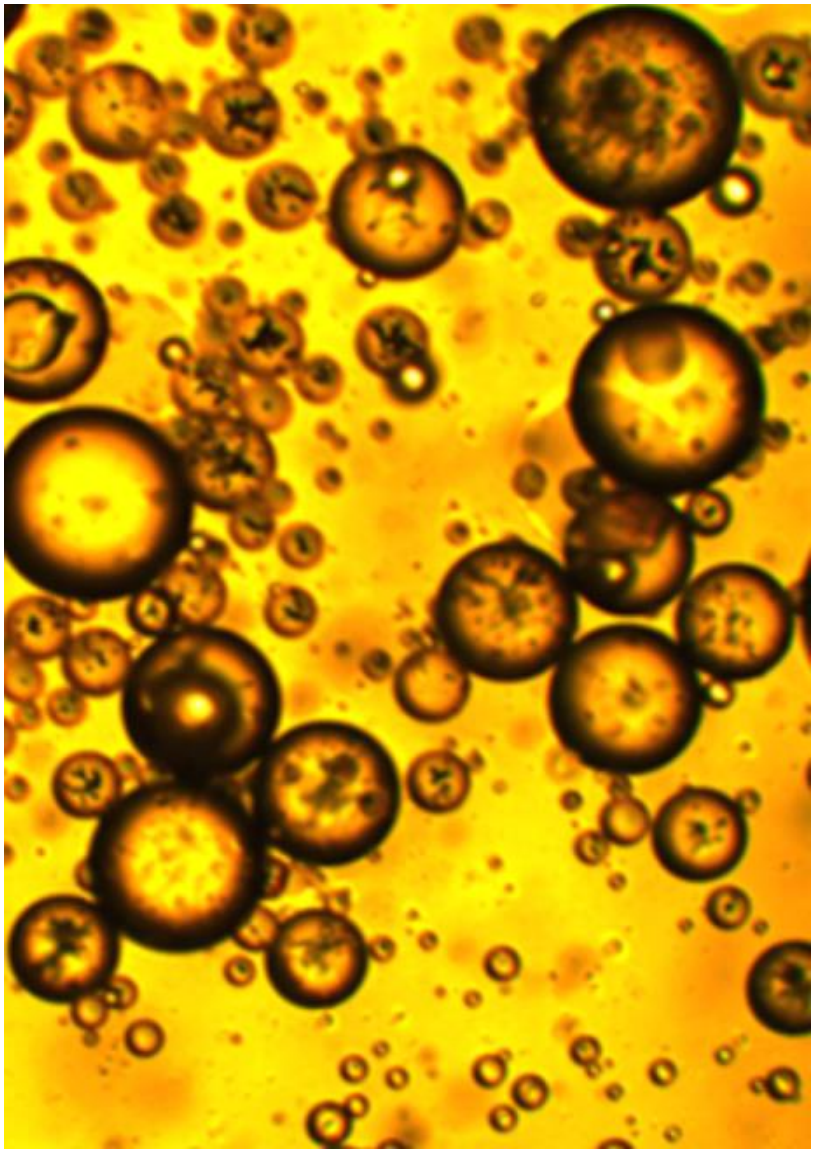
Technology Update – How Do We Control Methanogens?

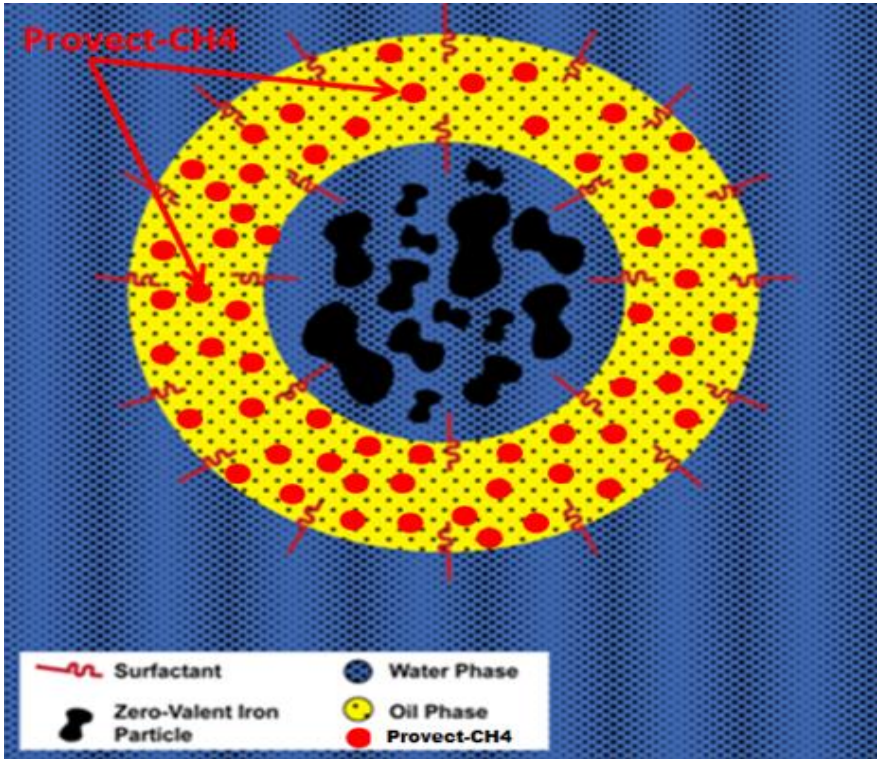
- Methanogens are genetically unique – ***Archaea***
- Utilizing naturally occurring statins (RYR Extract) and select essential oils/saponins to disrupt enzyme and coenzyme processes unique to methanogens





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





New product - **EZVI-CH4™**

Technology Update

Research & Development

Enhancing Product Implementability

EZVI Viscosity:

- Can be an issue for subsurface injections:
  - NASA patented formulation = ~ 1,200 – 1,900 cP
  - Provectus' low viscosity formulation = ~ 500 – 600 cP
    - R&D into viscosity adjustment is ongoing

Technology Update

Research & Development

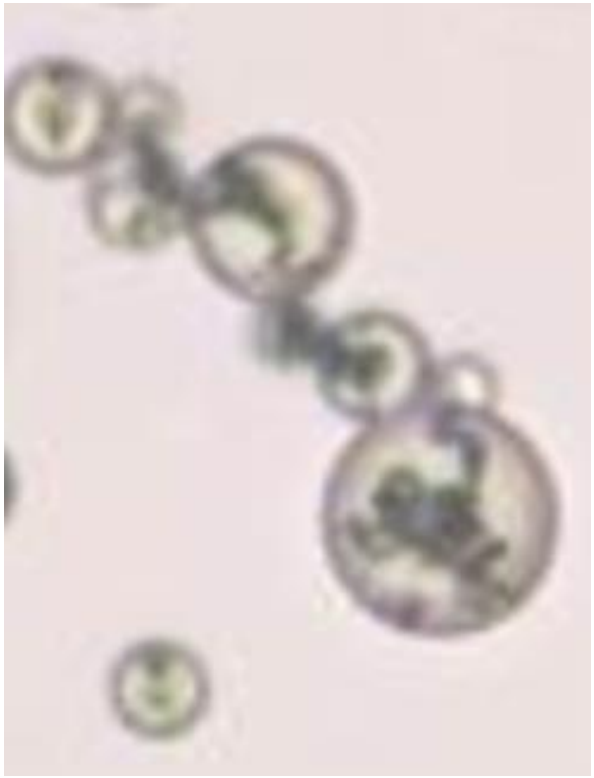
Optimizing Abiotic Processes

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



Cost & Benefit

Cost

- Varies based on product formulation and soil pore volume

Benefits

- Directly destroys halogenated contaminant source (DNAPL)
- Controlled methanogenesis with **EZVI-CH4™**
- 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 (~ 550 cP)
- The **STRUCTURE (water-in-oil type)** of the EZVI emulsion is key for the technology to perform as patented
- **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

<u>BOOTH 224</u>: Provectus Environmental Products, Inc.