Dispelling Myths and Extolling the Virtues of the EZVI Technology

Session D6: Advances in Amendment Formulation
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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)

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Presentation Outline

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

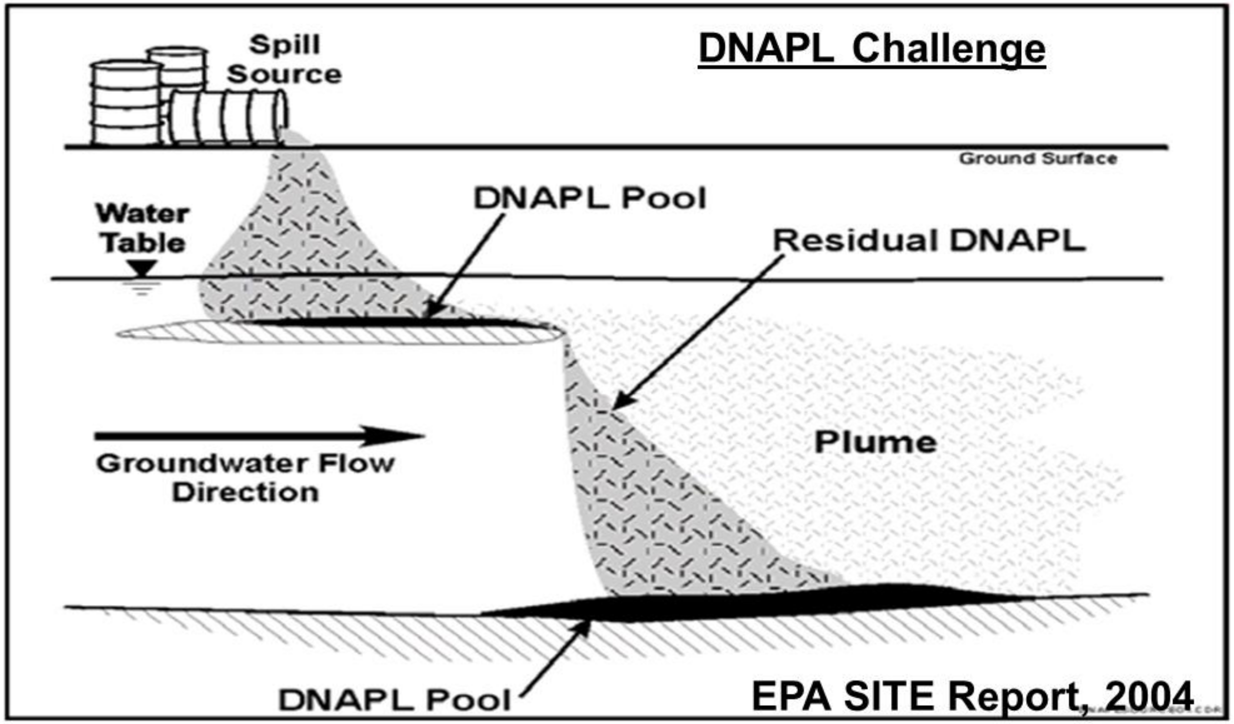
Presentation GOAL:

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

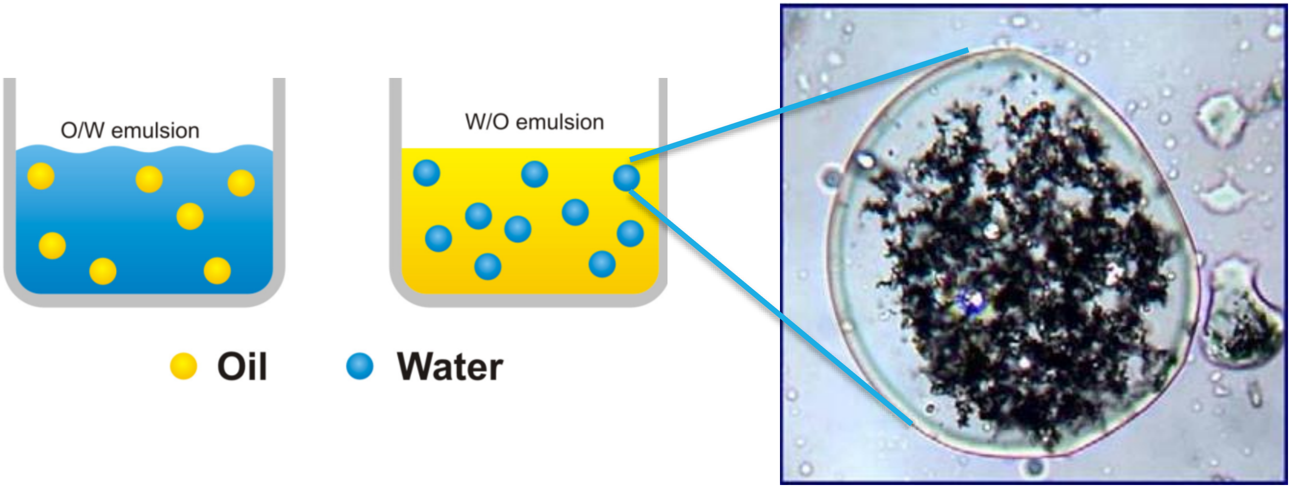
- 1997 – 1998: Conceptualization/Development
- 1999 – 2002: Proof of Concept R&D at UCF/KSC
- 2003 – 2004: Pilot studies – EPA SITE Evaluation
- **2005 – 1st FULL SCALE implementation – PAFB**
- 2005 – Present: Various Applications across USA, Canada, EU
- 2015 – Technology Enhancement – new product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

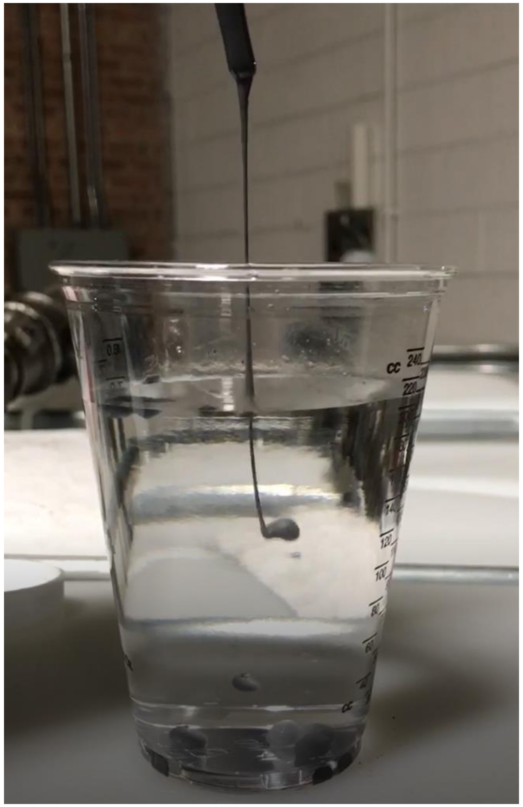
Technology Description

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)



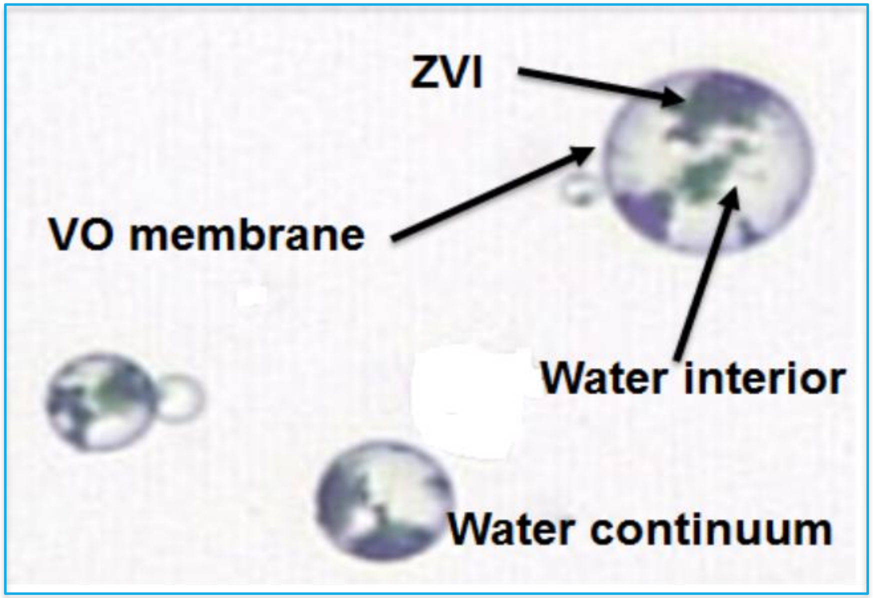


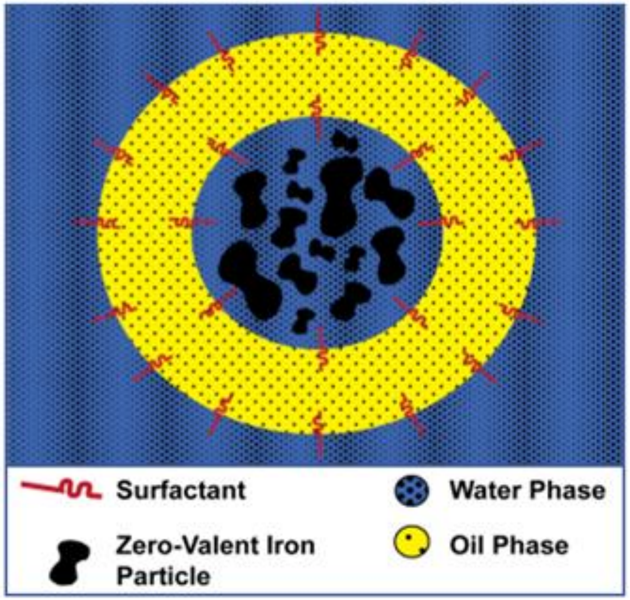
Technology Description

How does it work? -

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

Emulsion **Structure is KEY**

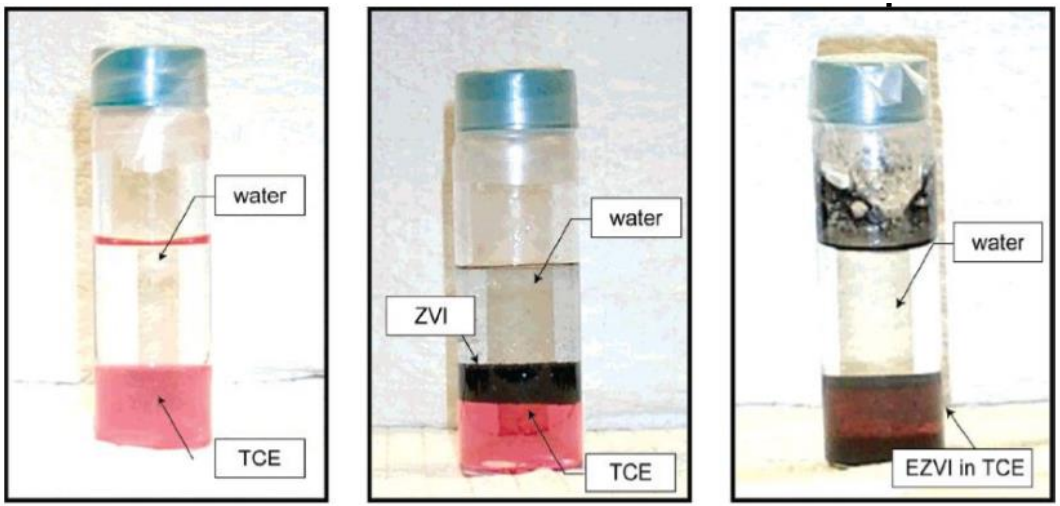




Technology Description

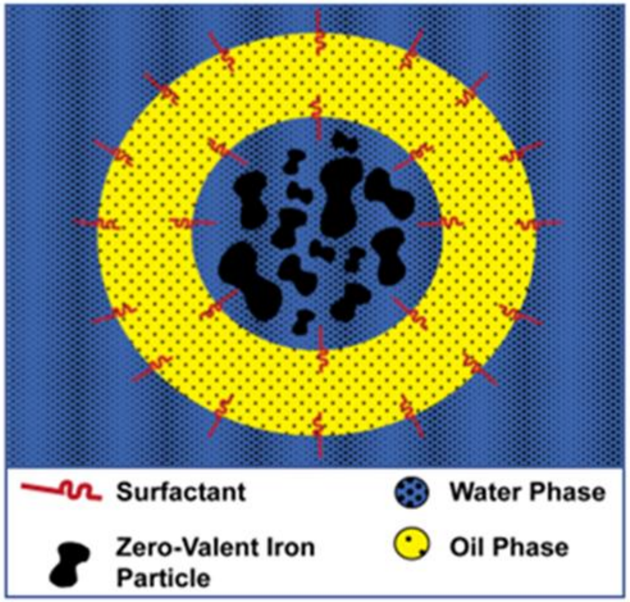
What is the innovation?

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



Miscible with DNAPL

Ref: Brooks et al., 2000

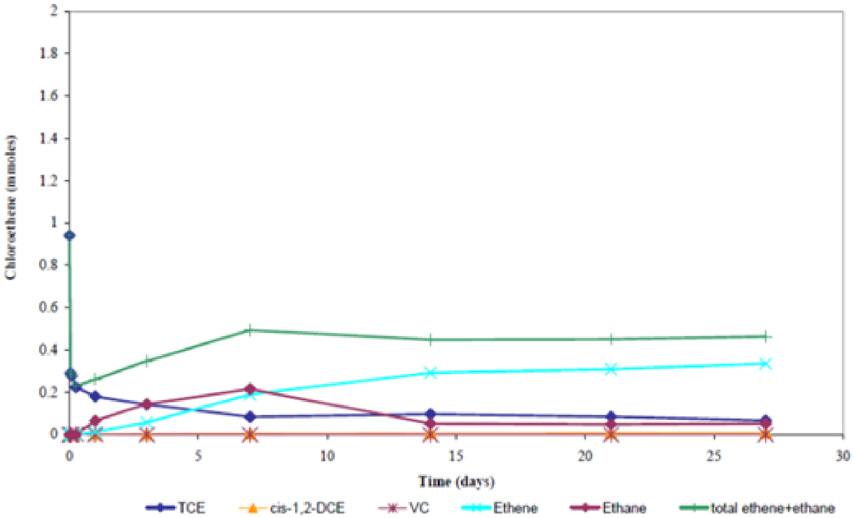


Technology Description

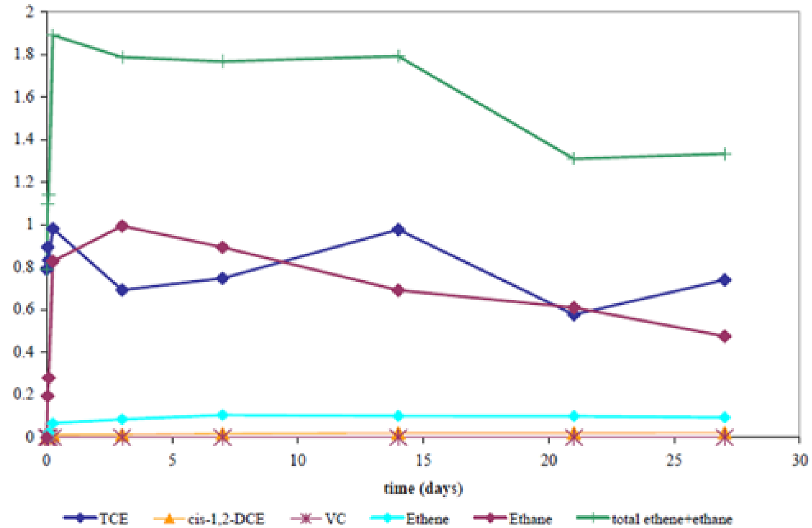
How is EZVI Unique?

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

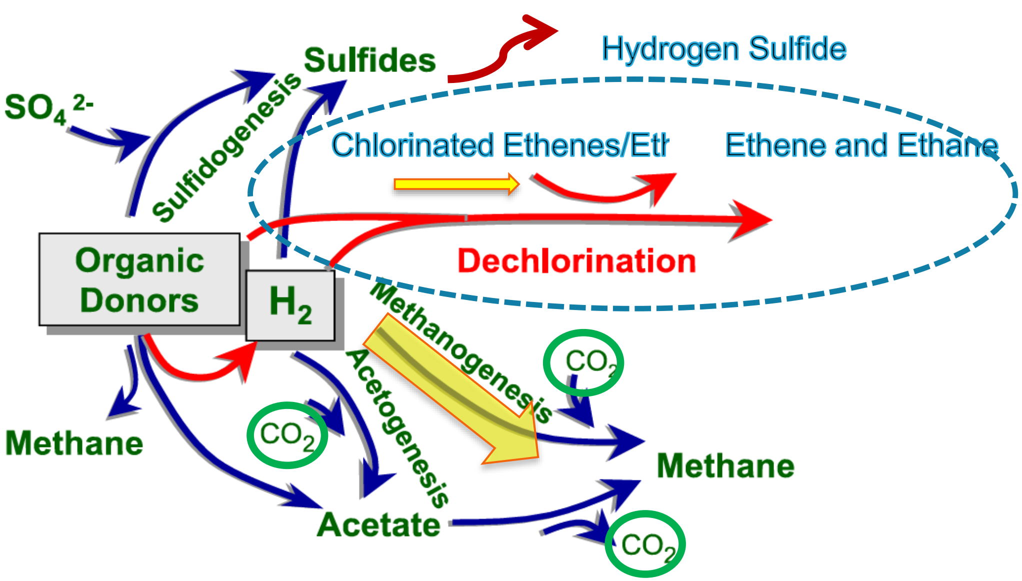
Is there a standard formulation?

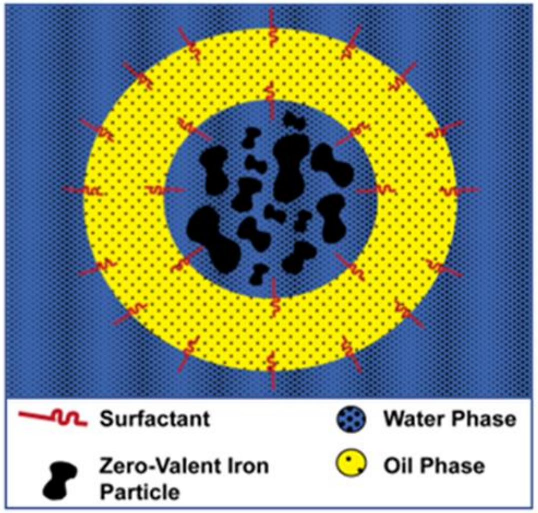
- Custom formulation is available
- Typical formula contains 10% ZVI (wt.%)

Technology Update – Hydrogen is the Currency

<u>Where Does it Go? = Cost and Efficiency Issues</u>: 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).

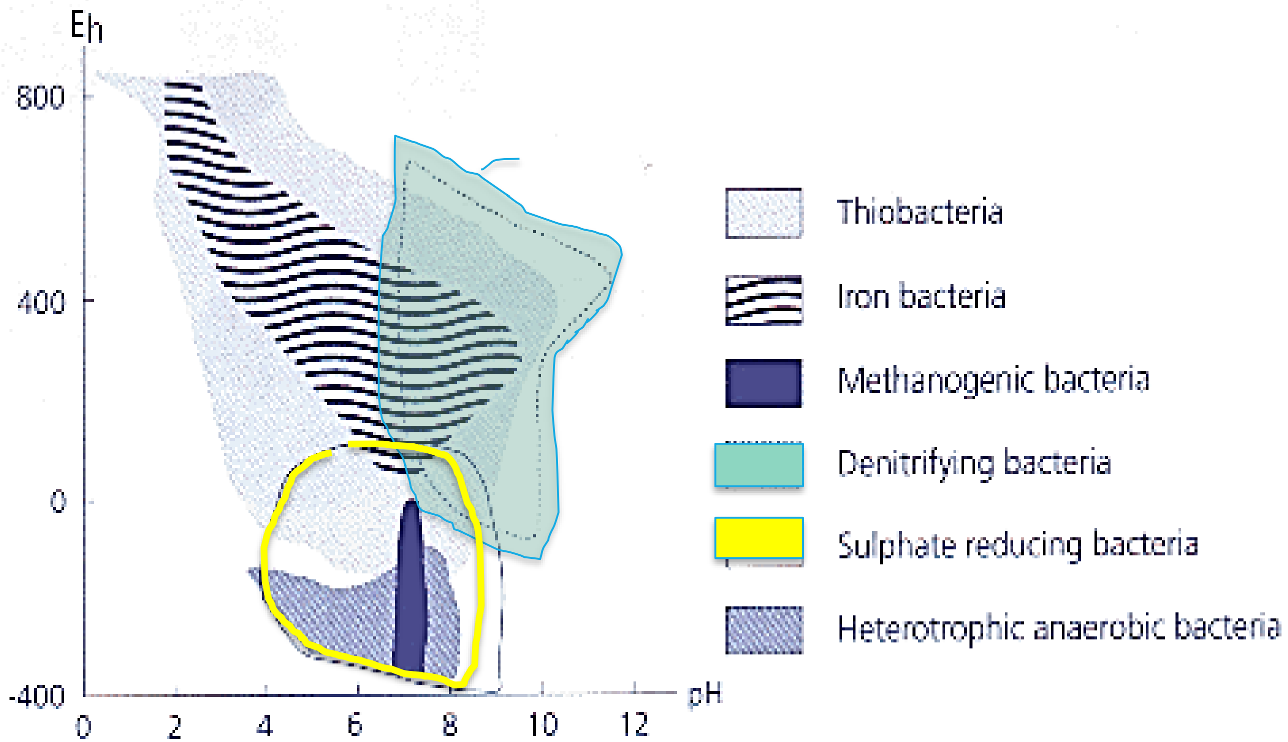
Optimizing Biological Processes





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?

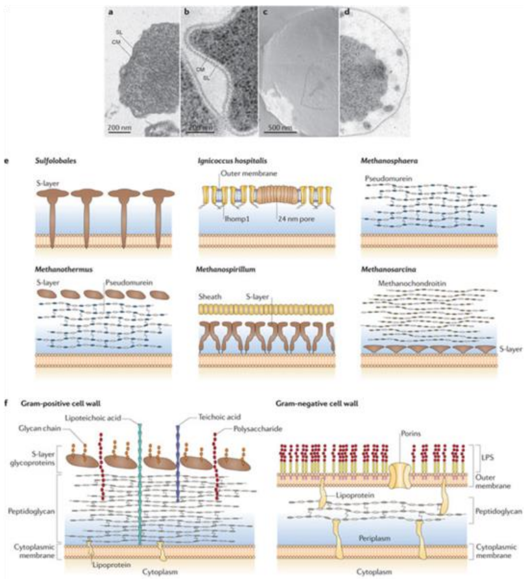
- **Cost and Efficiency Issues**: Production of methane is a direct indication that hydrogen generated from the electron donor amendments was used by methanogens instead of the target microbes (*e.g., Dehalococcoides spp*.), substantially reducing application efficiency.

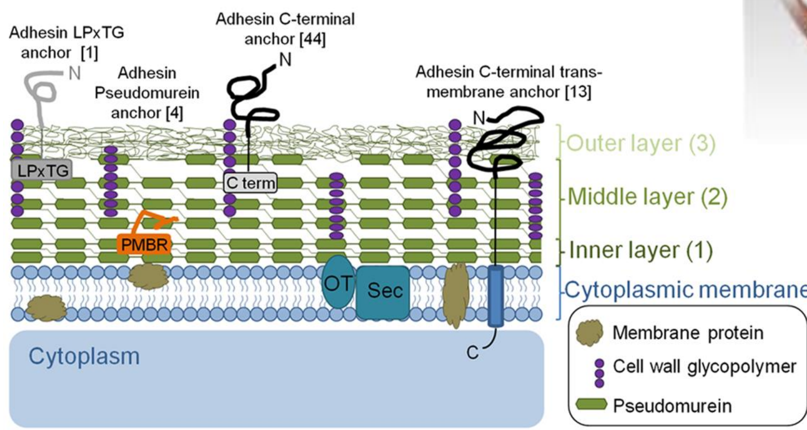
Constituent	Groundwater Concentration (mg/L)	Molecular Weight (g/mol)	Moles of H_2 to Reduce Mole Analyte	Moles of H_2 Acceptor In Treatment Area
Contaminant Electron Acceptors (To End Product Ethene)				
Tetrachloroethene (PCE)	10.0	165.8	4	1,393
Trichloroethene (TCE)	7.0	131.4	3	364
cis-1,2-Dichloroethene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

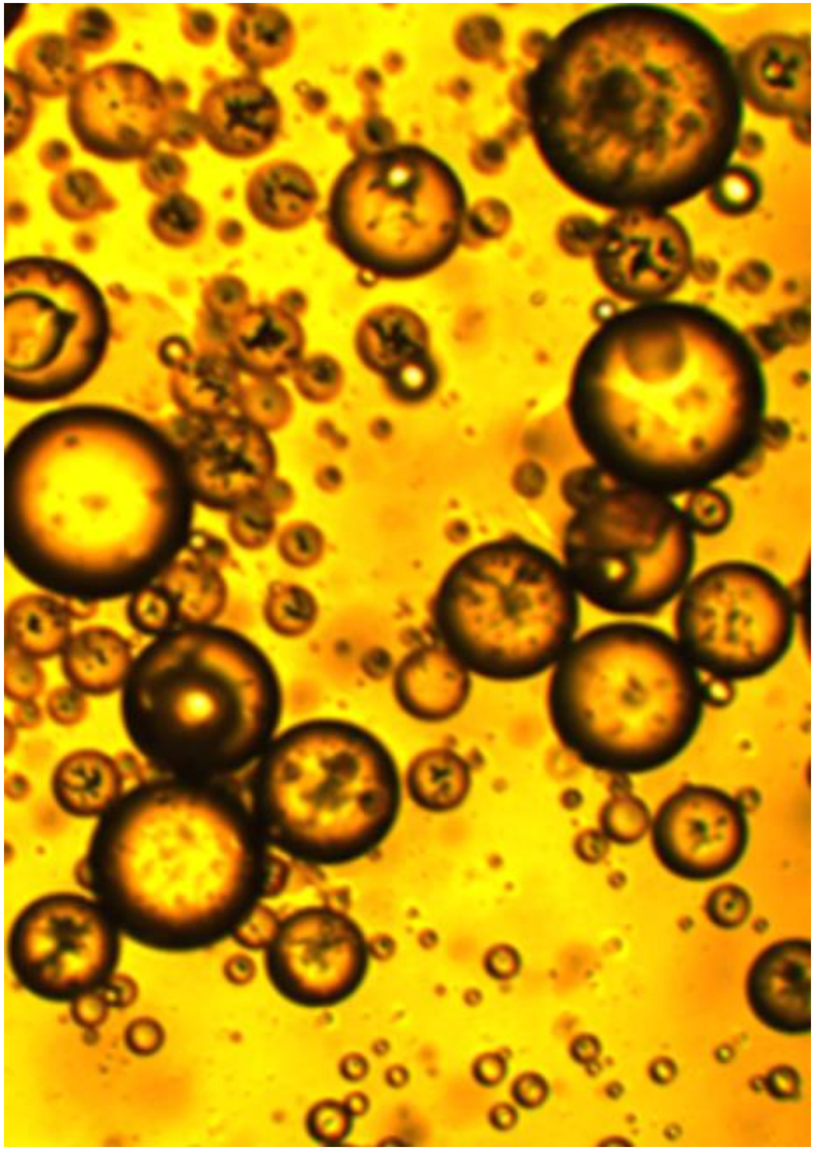
Technology Update – How Do We Control Methanogens?

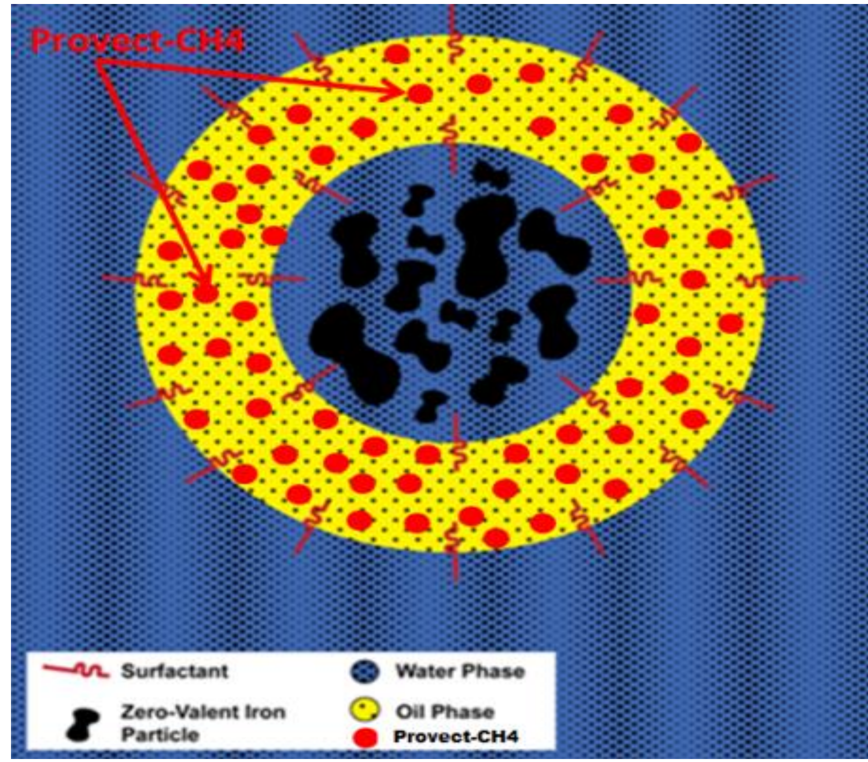
- Methanogens are genetically unique – ***Archaea***
- Utilizing naturally occurring statins (RYR Extract) and select essential oils/saponins to disrupt enzyme and coenzyme processes unique to methanogens





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





New product - **EZVI-CH4™**

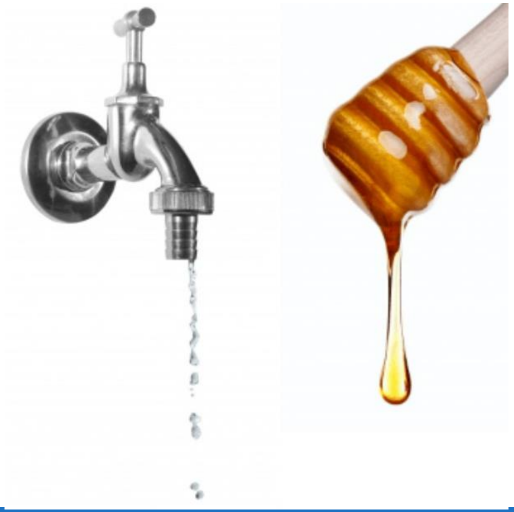
Technology Update

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

<u>Cost</u>

- Varies based on product formulation and soil pore volume

<u>Benefits</u>

- Directly destroys halogenated contaminant source (DNAPL)
- <u>Controlled methanogenesis</u> with **EZVI-CH4™**
- Effective in VADOSE soils
- Combination technology utilizes abiotic & biotic processes
- Utilizes contaminant physical chemistry to provide **significant reduction in source area <u>MASS FLUX</u>**

Summary

Newest Advancements to the EZVI technology:

- **EZVI-CH4™:** *In-situ* DNAPL destruction with **controlled methanogenesis** and **lower viscosity** (~ 550 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.

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