



Dispelling Myths and Extolling the Virtues of the EZVI Technology

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

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6/12/2017

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:

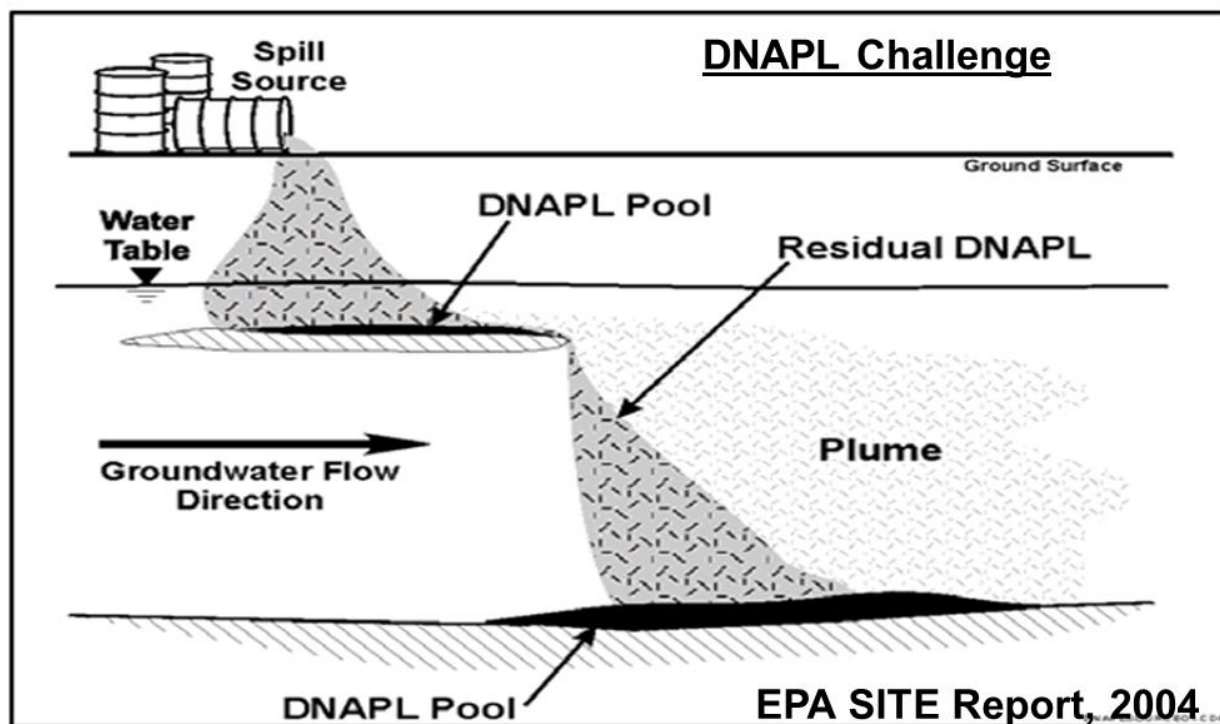
For you to gain a good understanding of what the EZVI technology is (and isn't), when it is an appropriate remedial alternative and what are the most recent advancements to the technology.

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

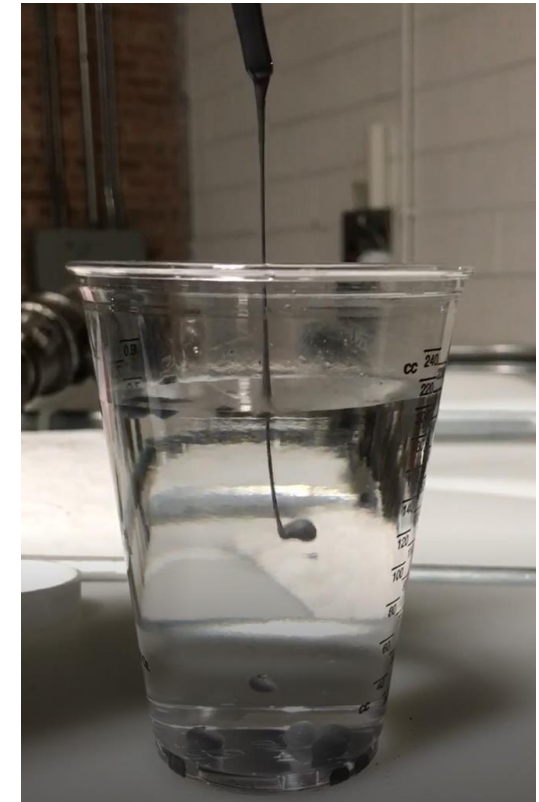
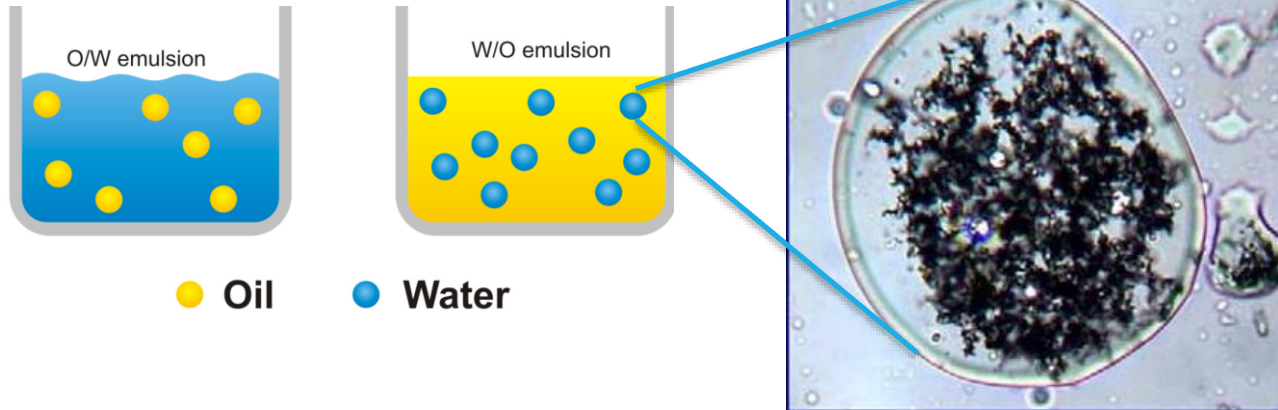
- 1997 – 1998: Conceptualization/Development
- 1999 – 2002: Proof of Concept R&D at UCF/KSC
- 2003 – 2004: Pilot studies – EPA SITE Evaluation
- **2005 – 1st FULL SCALE implementation – PAFB**
- 2005 – Present: Various Applications across USA, Canada, EU
- 2015 – Technology Enhancement – new product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



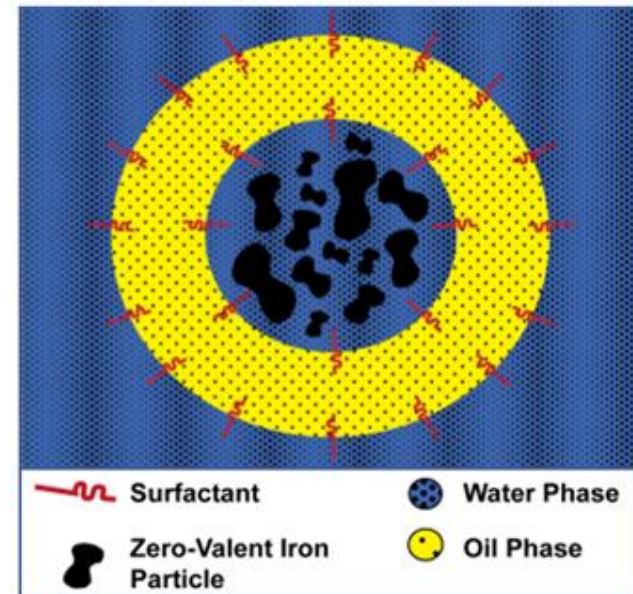
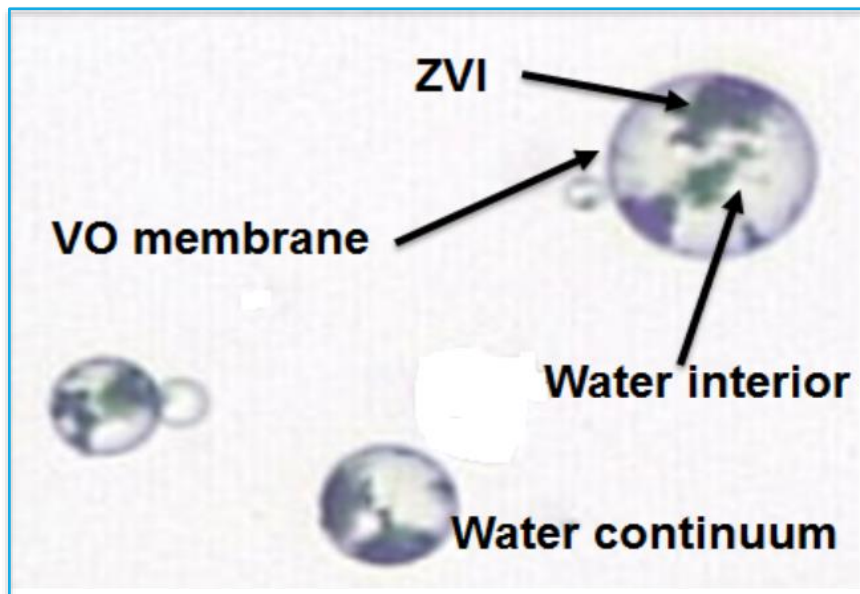
Technology Description



How does it work? -

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

Emulsion Structure is KEY

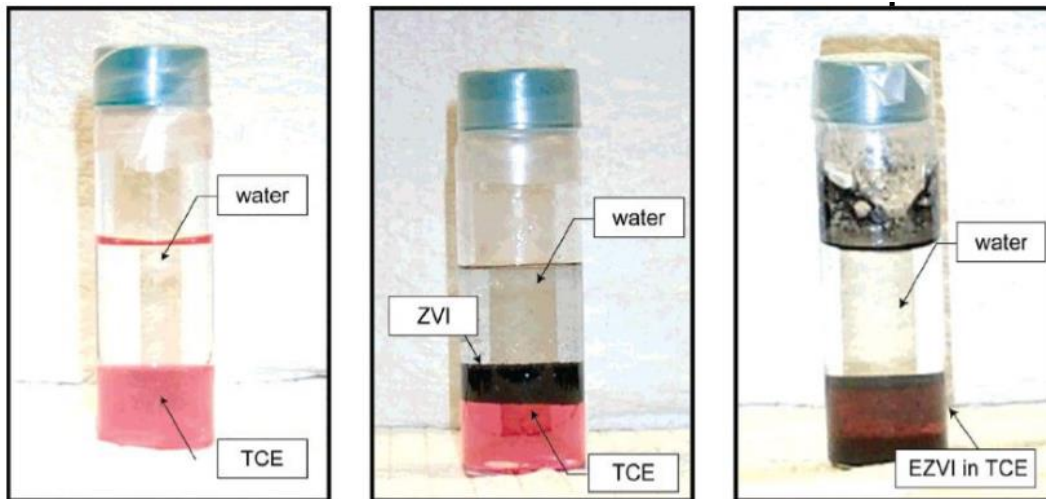


Technology Description



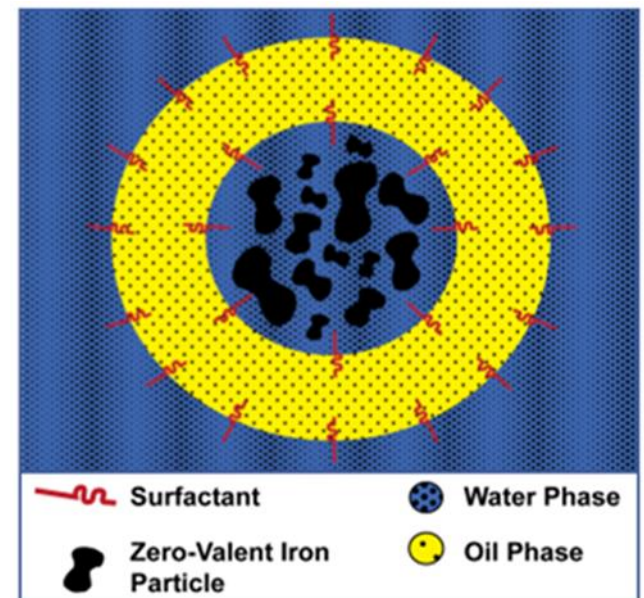
What is the innovation?

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



Miscible with DNAPL

Ref: Brooks et al., 2000



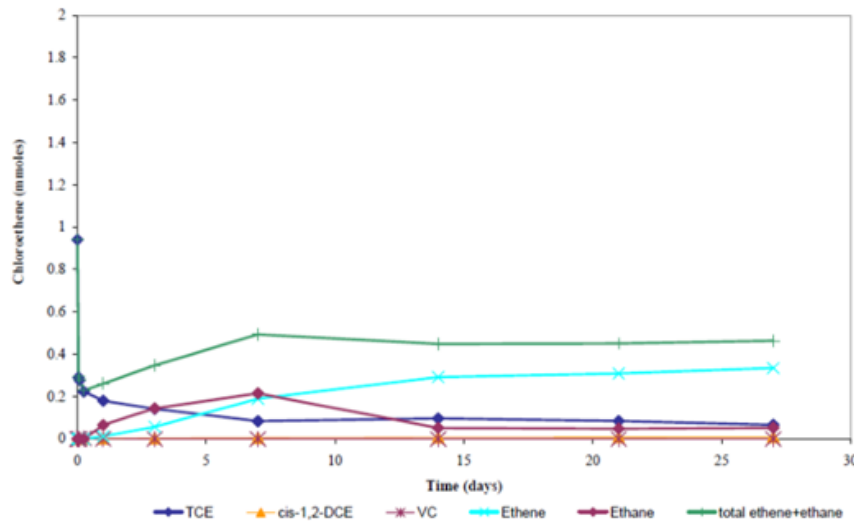
Technology Description



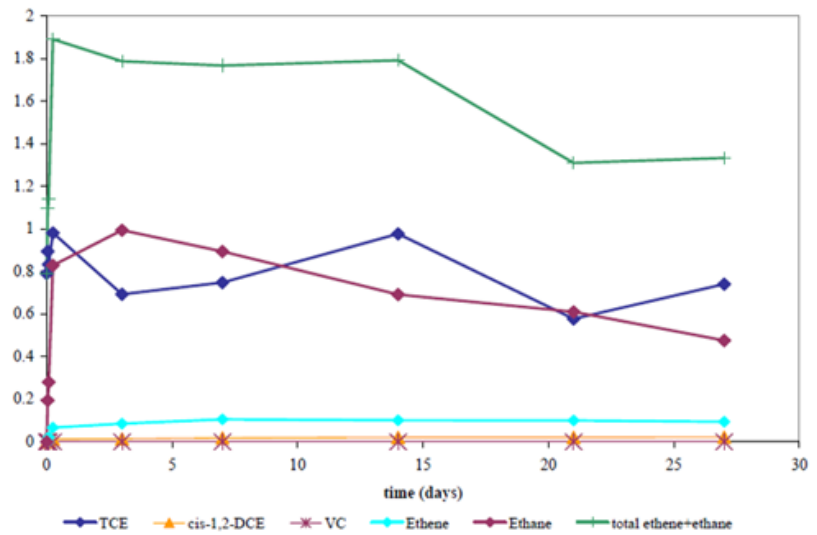
How is EZVI Unique?

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 \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

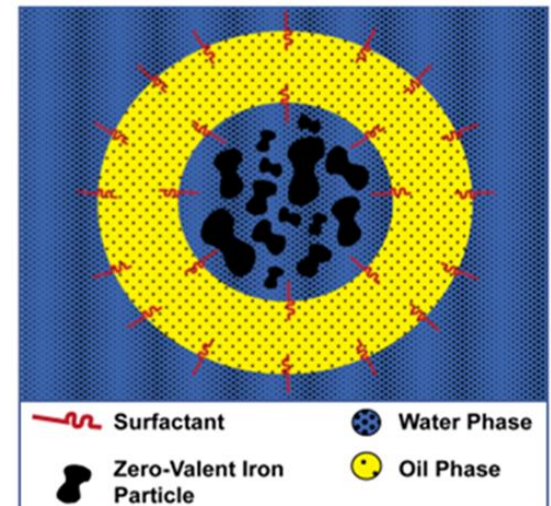
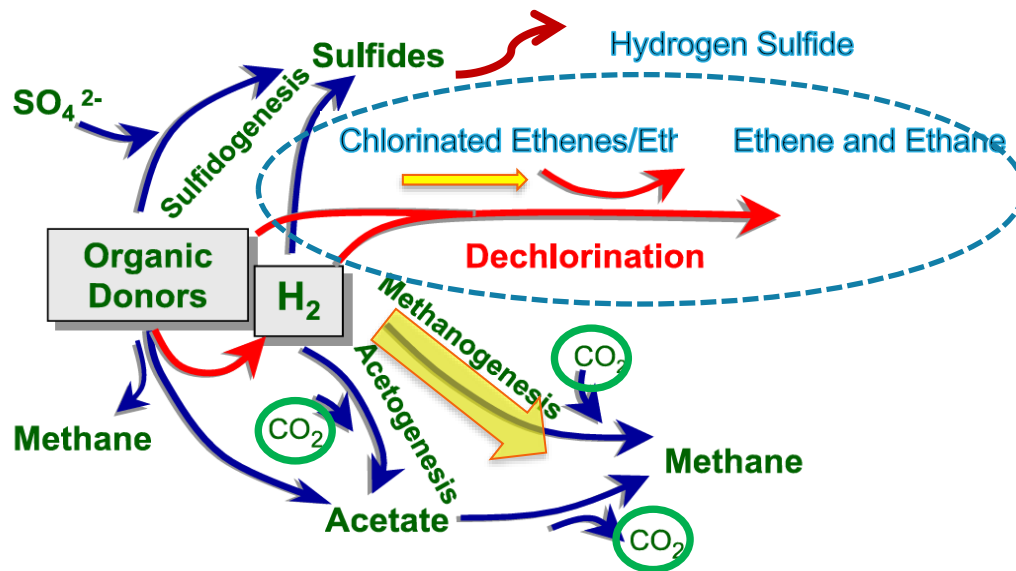
Is there a standard formulation?

- 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 Provectus).

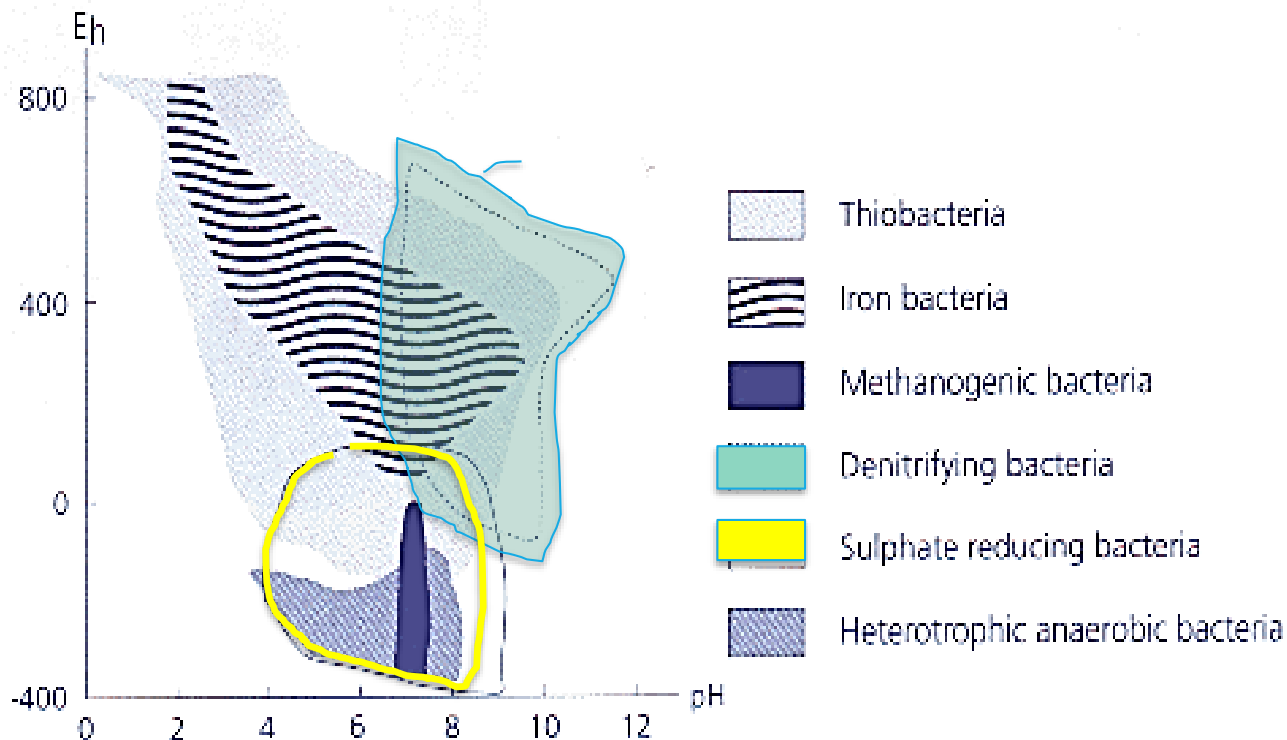
Optimizing Biological Processes



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



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.

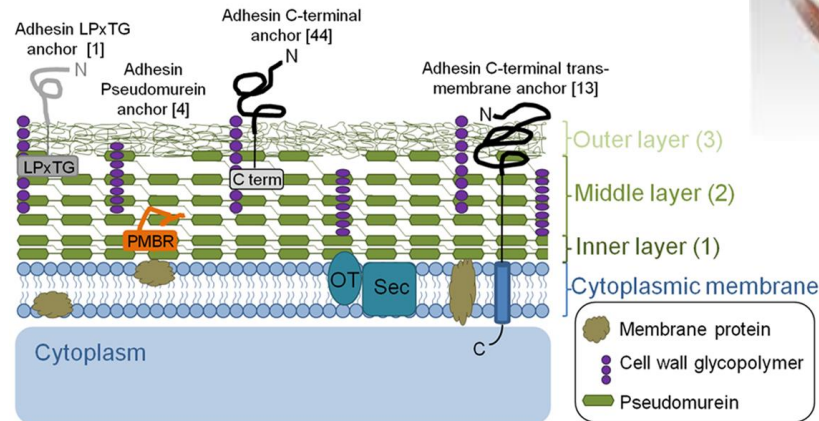
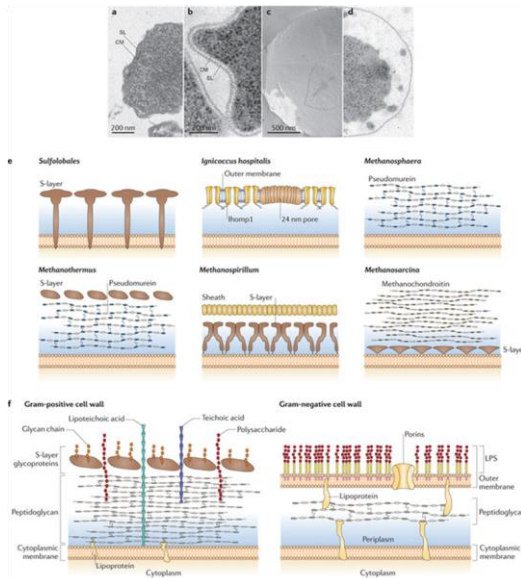
Constituent	Groundwater Concentration (mg/L)	Molecular Weight (g/mol)	Moles of H ₂ to Reduce Mole Analyte	Moles of H ₂ Acceptor In Treatment Area
Contaminant Electron Acceptors (To End Product Ethene)				
Tetrachloroethene (PCE)	10.0	165.8	4	1,393
Trichloroethene (TCE)	7.0	131.4	3	364
cis-1,2-Dichloroethene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

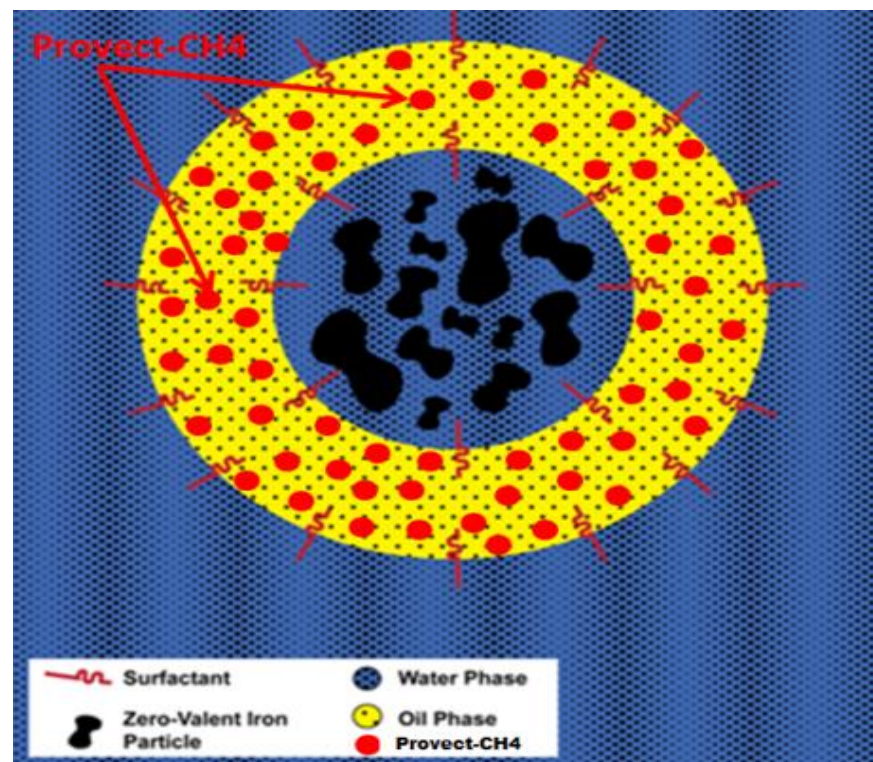
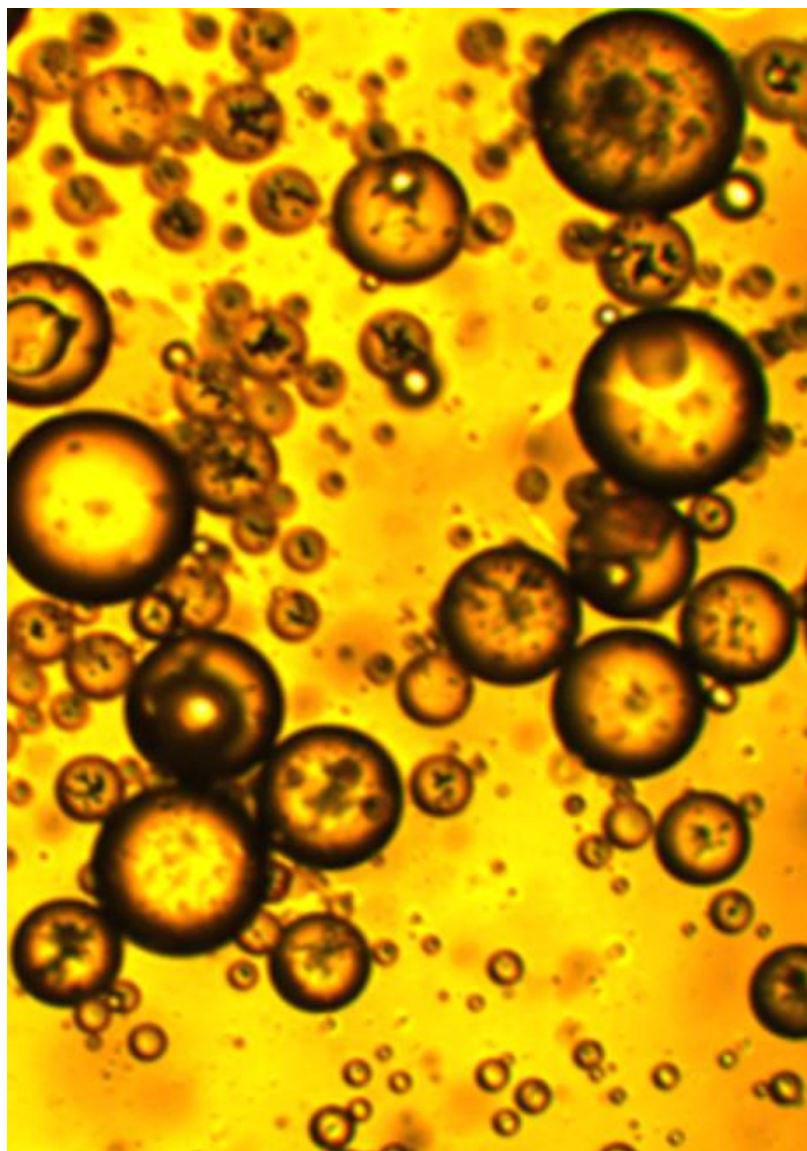
Technology Update – How Do We Control Methanogens?



- Methanogens are genetically unique – **Archaea**
- Utilizing naturally occurring statins (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™**

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 = $\sim 500 - 600$ 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



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**

Newest Advancements to the EZVI technology:

- **EZVI-CH₄TM:** *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

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