# Catalyzed Enhanced Reductive Bioremediation

Wednesday, May 3, 2023

12:00 PM - 1:00 PM EDT

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# Agenda

**01** Bioremediation
Biological Reductive Dechlorination

**02** Emulsified Vegetable Oils
History and Advancements

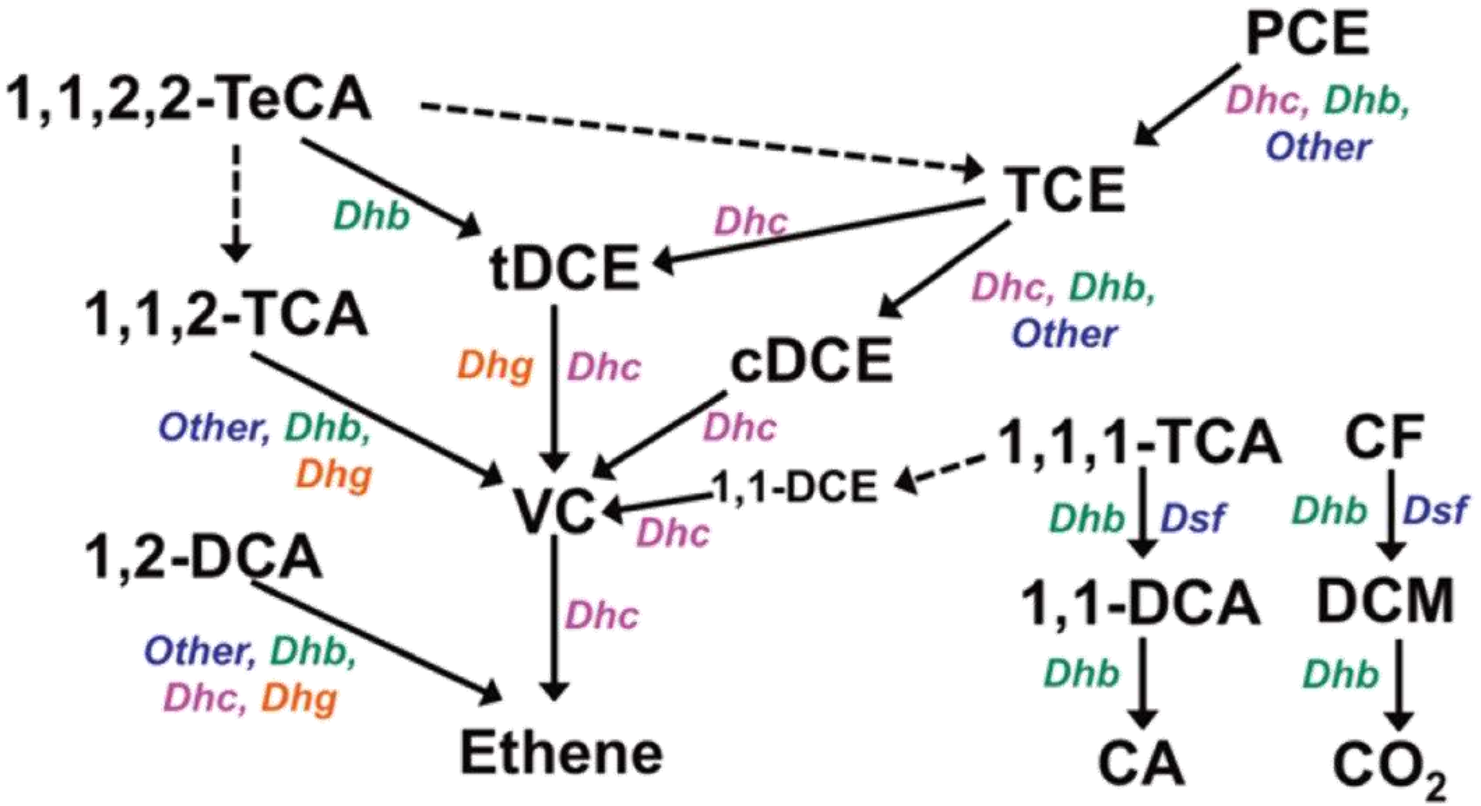
**03** Catalyzed Enhanced Reductive Bioremediation
Transesterification of Vegetable Oils

**04** Enhancement Options
Benefits of this approach

# What is needed for enhanced reductive dechlorination?

**Vegetable oils ferment to acetic acid and hydrogen**

# Overview: chlorinated solvent dechlorination pathways and organisms responsible




Dhc = Dehalococcoides
Dhg = Dehalogenimonas
Dhb = Dehalobacter
Other = e.g., Desulfitobacterium (Dsf), Sulfurospirillum, Geobacter
----- Dashed lines are abiotic reactions

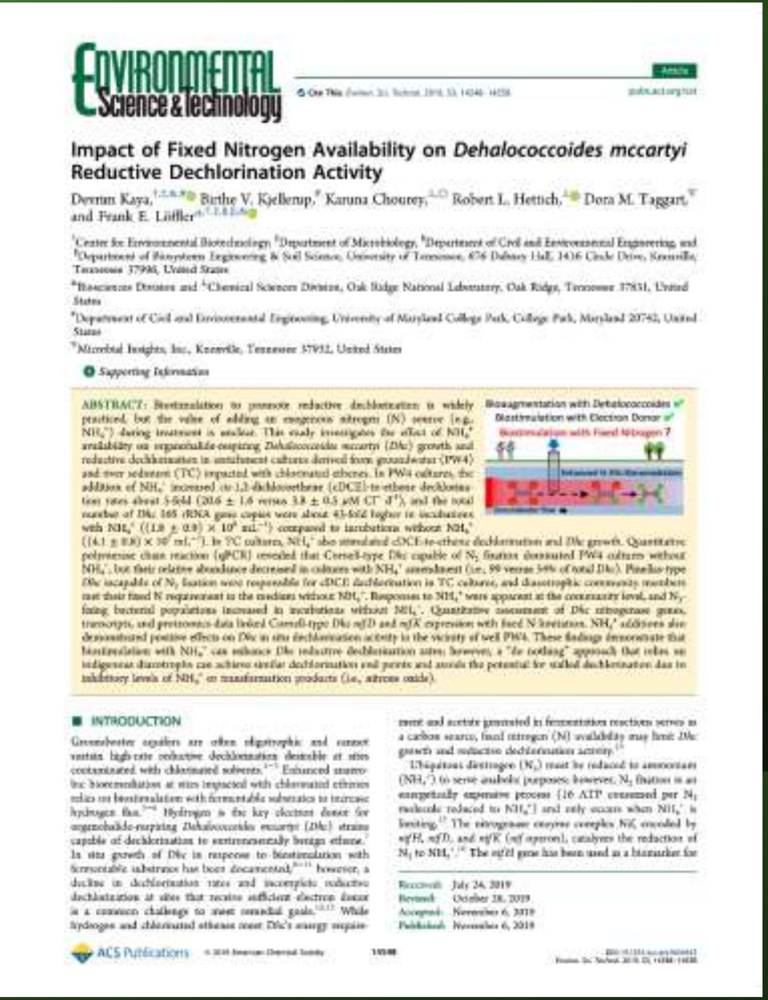
Wei K., Grostern A., Chan W.W.M., Richardson R.E., Edwards E.A. (2016) Electron Acceptor Interactions Between Organohalide-Respiring Bacteria: Cross-Feeding, Competition, and Inhibition. In: Adrian L., Löffler F. (eds) Organohalide-Respiring Bacteria. Springer, Berlin, Heidelberg. https://doi.org/10.1007/978-3-662-49875-0_13

# *EDS-ER™*

## Electron Donor Solution – Extended Release

Water soluble vegetable oil

USDA CERTIFIED BIOBASED PRODUCT
PRODUCT 99%
FP


Environmental Science & Technology

Impact of Fixed Nitrogen Availability on *Dehalococcoides mccartyi* Reductive Dechlorination Activity

Devrim Kaya, Birthe V. Kjellerup, Karuna Chourey, Robert L. Hettich, Dora M. Taggart, and Frank E. Löffler

Supporting Information

*Environ. Sci. Technol.* 2019, 53, 24, 14548−14558

# Nutrients

- Biostimulation benefits from adding an exogenous nitrogen (N) source (e.g., $NH_4^+$)
- Addition of $NH_4^+$ increased cis-1,2-dichloroethene (cDCE)-to-ethene dichlorination rates about 5-fold
- Typical target dosing:
  - 20:1 BOD to $NH_3$ – N ratio
  - 100:1 BOD to $PO_4$ – P ratio

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# TersOx™ Nutrients-QR


- Fast-acting soluble nutrient blend for bioremediation
- Blend of nitrogen, phosphorous and microbial growth enhancers that provide a source of urea, phosphate and potassium

# Vitamin $B_{12}$

- *Dehalococcoides mccartyi strains* require vitamin $B_{12}$ (Yan et al, 2013)
- Reported concentration for optimal dechlorination and growth: 25 to 50 µg/L (Stroo et al., 2013)

Stroo et al., 2013, Bioaugmentation for Groundwater Remediation, edited by Stroo, H.F., Leeson, A., Ward, C.H. HydroGeoLogic, Inc., Ashland, OR, USA

Yan et al, 2013, Yan J, Im J, Yang Y, Löffler FE. 2013 Guided cobalamin biosynthesis supports *Dehalococcoides mccartyi* reductive dechlorination activity. Phil Trans R Soc B 368: 20120320. http://dx.doi.org/10.1098/rstb.2012.0320


Tote Photograph Curtesy of Legacy Remediation, Inc.

# Distribution of the Correct Type of Fatty Acids is Essential

**Acetate**

- Slow consumption
- Will migrate downgradient
- Stimulates PCE -> TCE -> cDCE
- Will not stimulate cDCE -> VC -> ethene

**Hydrogen ($H_2$)**

**Produced from linolenic acid, propionate, butyrate, etc.**

- Rapid consumption
- Does not migrate beyond injection zone
- Required for cDCE -> VC -> ethene


(12) United States Patent
Birk et al.

(10) Patent No.: US 11,577,231 B2
(45) Date of Patent: Feb. 14, 2023

(54) ENHANCED REDUCTIVE BIOREMEDIATION METHOD USING IN-SITU ALCOHOLYSIS

(71) Applicant: Tersus Environmental LLC, Wake Forest, NC (US)

(72) Inventors: Gary M. Birk, Wake Forest, NC (US); David F. Alden, Scranton, PA (US)

(73) Assignee: Tersus Environmental LLC

(21) Appl. No.: 16/797,617

(22) Filed: Feb. 21, 2020

Prior Publication Data

(51) Int. Cl.

(52) U.S. Cl.

(58) Field of Classification Search

(56) References Cited

U.S. PATENT DOCUMENTS

FOREIGN PATENT DOCUMENTS

OTHER PUBLICATIONS

* cited by examiner

(57) ABSTRACT

20 Claims, 5 Drawing Sheets

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# Deploying Electron Donor via *In Situ* Alcoholysis

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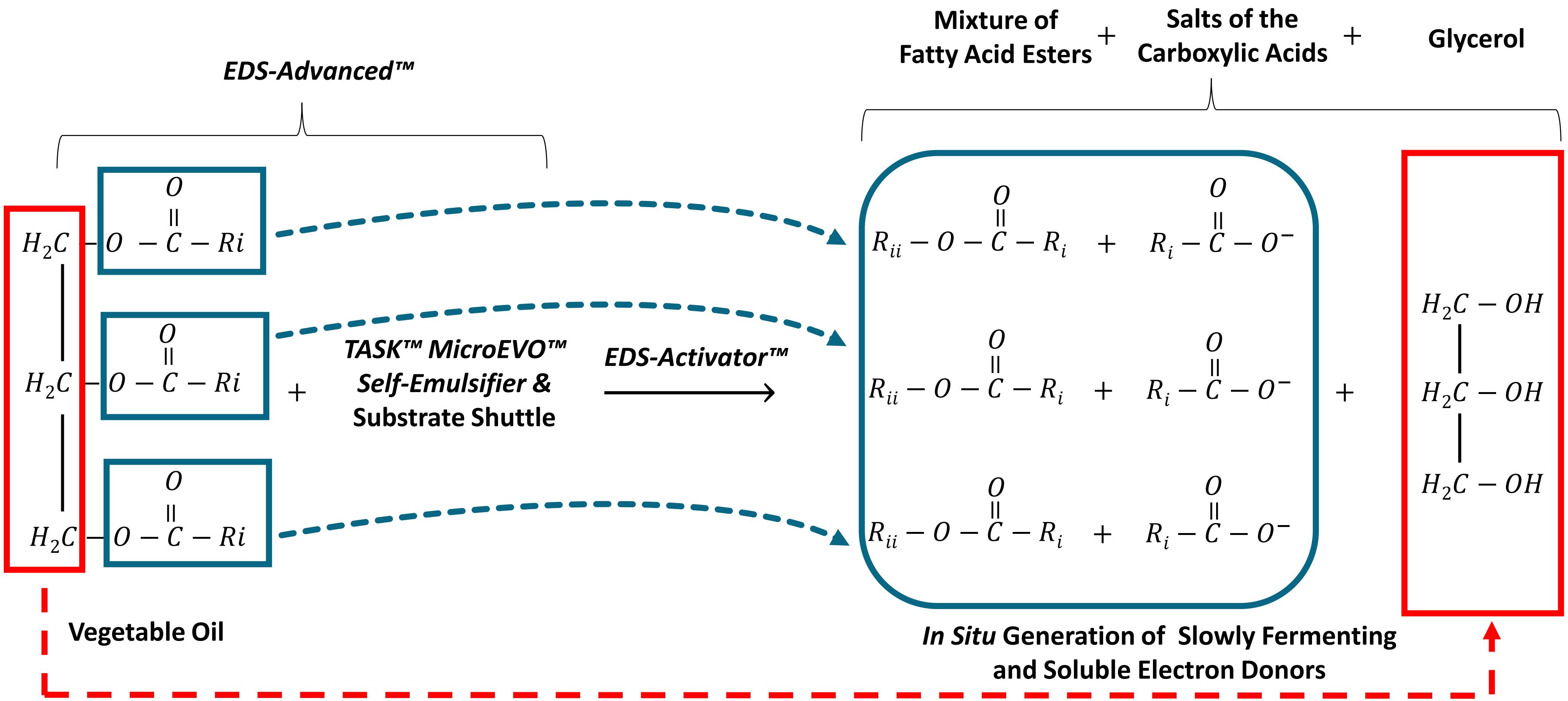
# Definitions

- <u>Alcoholysis</u>: A reaction in which an alcohol is a reactant and becomes part of the reaction product.
- <u>Transesterification</u>: The chemical conversion process of triglycerides with alcohol into fatty acid esters with the help of a catalyst.

# *In Situ* Transesterification of Vegetable Oils



# Activator Options

**Hydroxide base-catalyzed transesterification of triglycerides**

- Homogeneous Alkaline Catalyst
    - Alkyl oxides ($RO^-$)

**Lipase-catalyzed hydrolysis of triglyceride**

- Biocatalyst
    - Enzyme (triglyceride lipases)

# pH Plays a Key Role in VFA Production

**Systems under alkaline conditions**

- Enhances the activity of fatty acid-producing bacteria
- Inhibits methanogens
- Increases production of VFAs

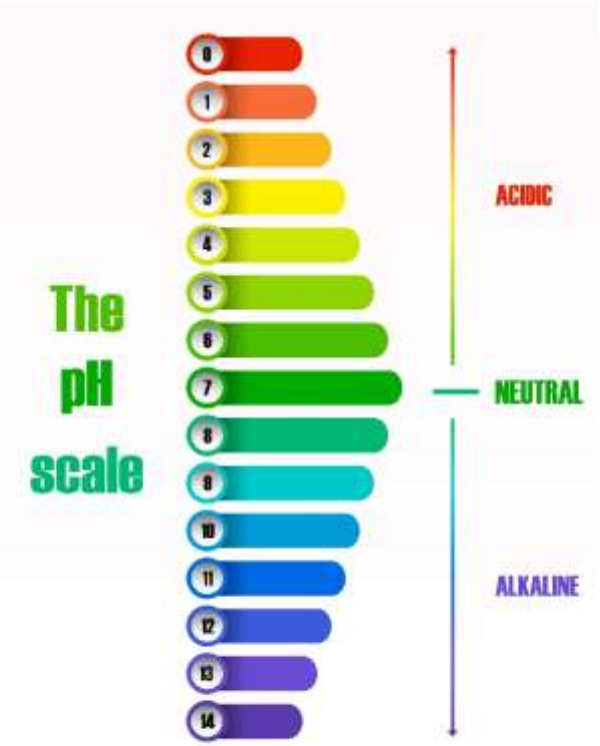



Image by brgfx on Freepik,
www.freepik.com/free-vector/ph-scale-diagram_4453068.htm

# Typical Application Rates

| | |
|---|---|
| EDS-ER™ (Soybean Oil and TASK™ MicroEVO™ Self-Emulsifier | 6 to 8 g/L |
| EDS-Activator™ | 16 to 20% of EDS-ER™ Dose |
| EDS Substrate Shuttle (Co-Solvent) | 0.4 g/L |
| EDS-ME™ (Alcohol Blend) | 0 to 2.4 g/L* |

*Based on average sum of chlorinated solvents across treatment zone

# Example Projects

# TCE Site

- 2,830 µg/L TCE (highest conc.)
- Primawave® Pressure Pulse
- Injected 75,000L of EDS-Advanced™ into the source zone over two weeks


Photos curtesy of Justin Kerr, Kerr Environmental, Greater Adelaide Area, SA, AUSTRALIA

# Injection Setup

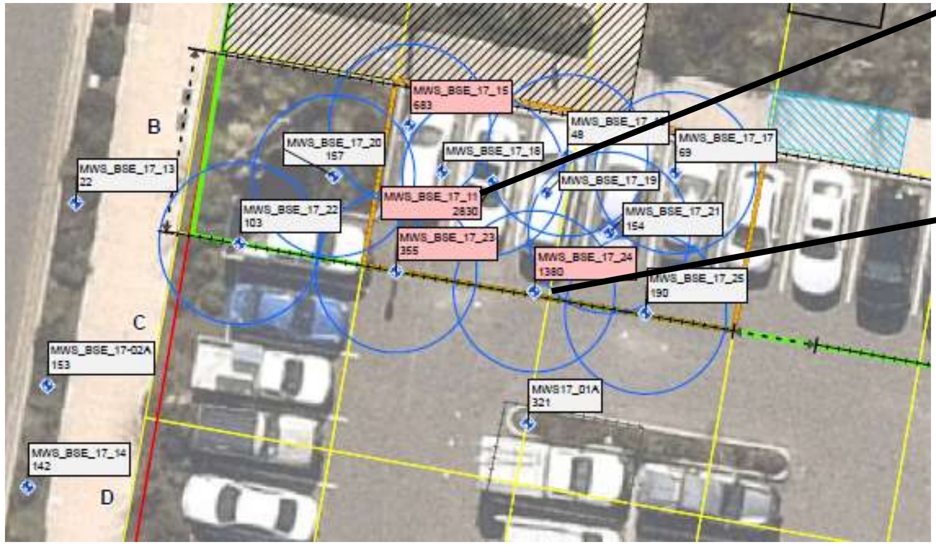
**Four injection lines with individual flow and pressure control and monitoring**

**Primawave® Pressure Pulse**

**for injection into clays**

Photos and video curtesy of Justin Kerr, Kerr Environmental, Greater Adelaide Area, SA, AUSTRALIA

# TCE Results
## (Approximately 95% mass reduction)

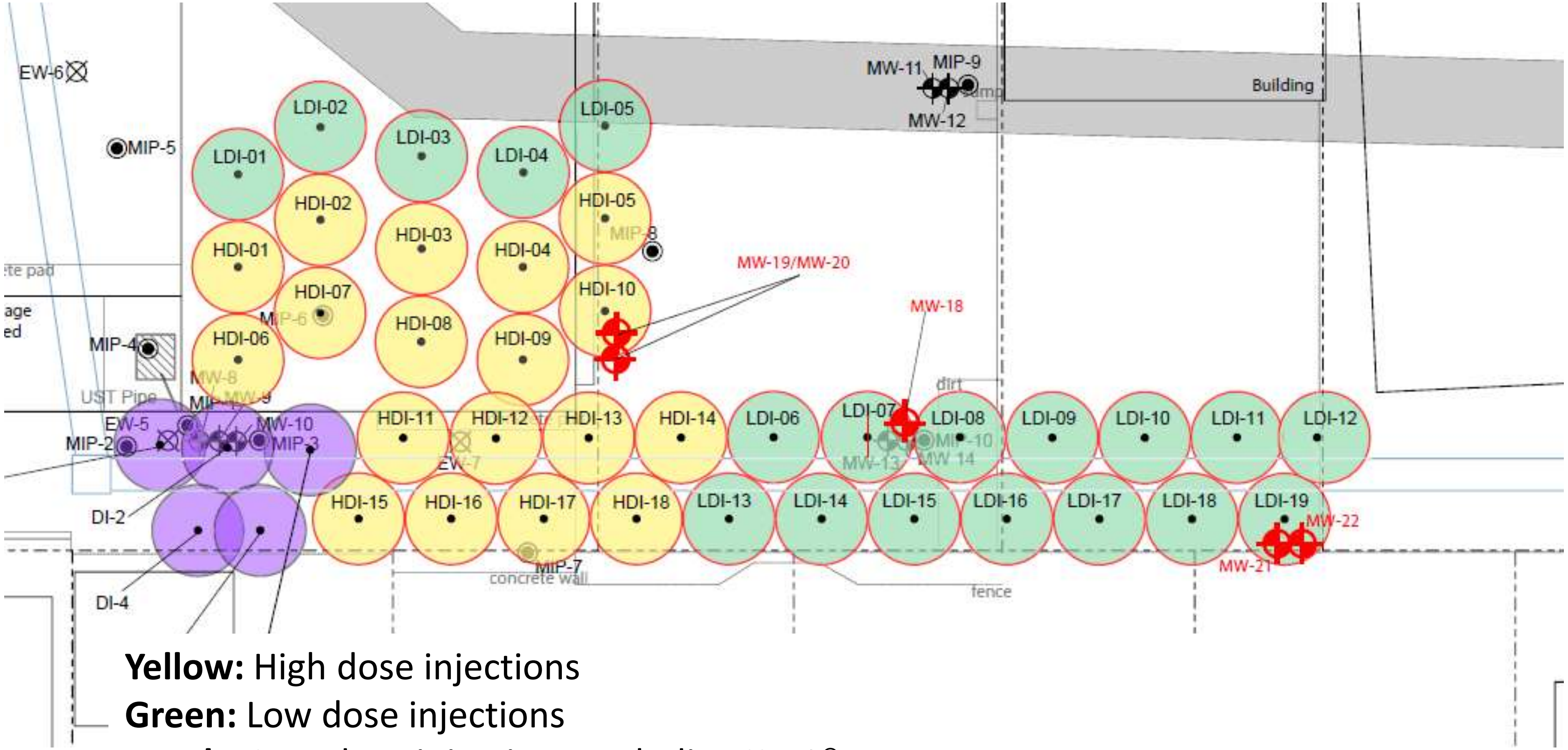



Data curtesy of Justin Kerr, Kerr Environmental, Greater Adelaide Area, SA, AUSTRALIA

**MWS_BSE_17_11**
Baseline 2,830 µg/L
Week 13 33.1 µg/L

**MWS_BSE_17_24**
Baseline 1,380 µg/L
Week 13 55.8 µg/L

# TCE Site



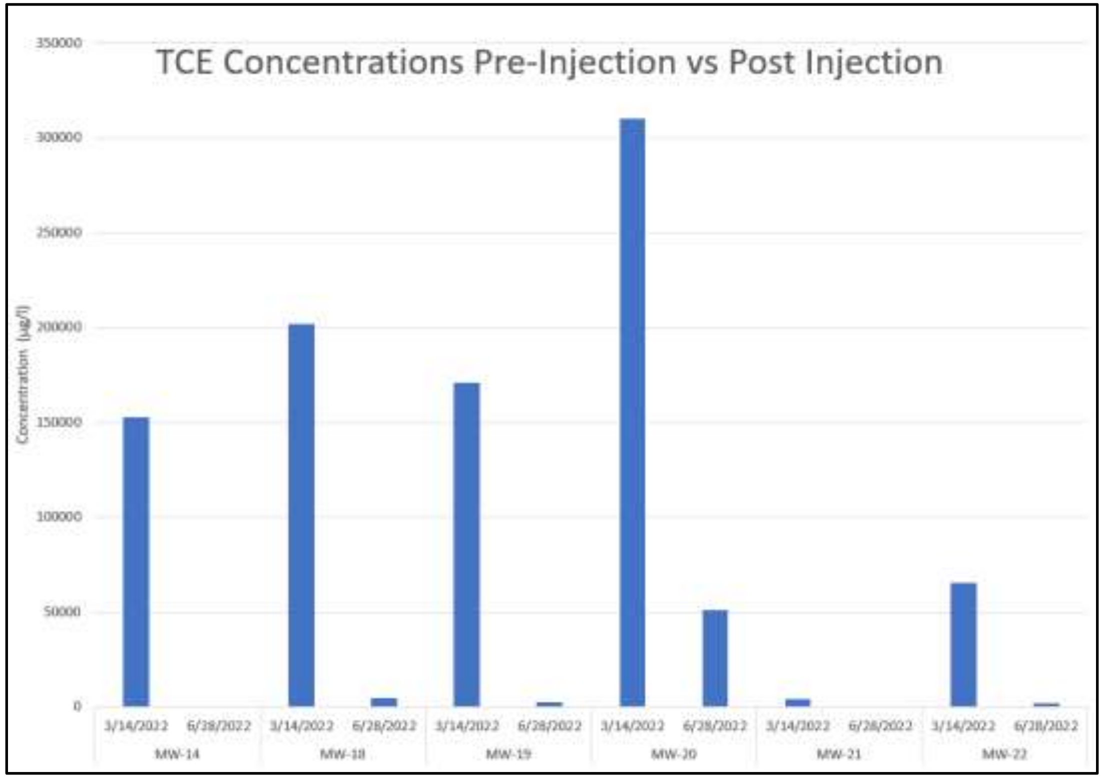

**Yellow:** High dose injections

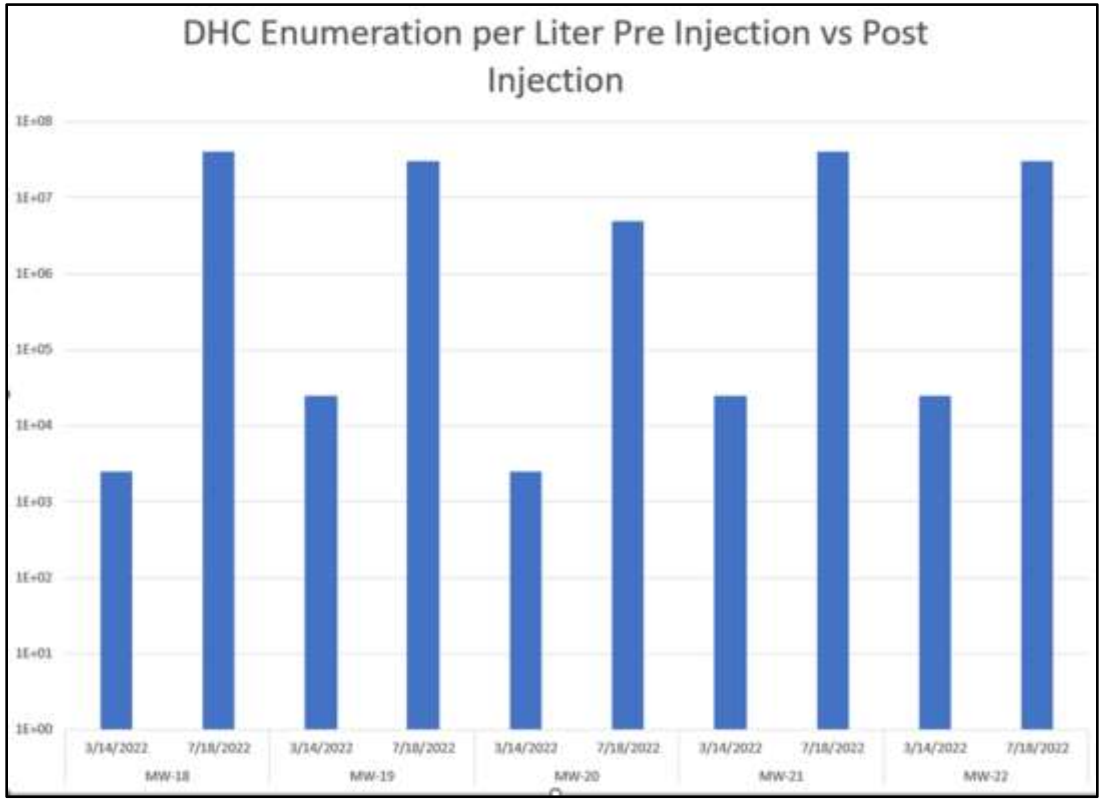
**Green:** Low dose injections

**Purple:** Low dose injections excluding KB-1®

Reference: Remediation Seminars Webinar, *How to Integrate Bench Scale Tests, Molecular Diagnostic Tools (MDT), and Compound-Specific Isotope Analysis (CSIA) to you Field Pilot Test*, Dec. 7, 2022

# Injection Results




Reference: Remediation Seminars Webinar, *How to Integrate Bench Scale Tests, Molecular Diagnostic Tools (MDT), and Compound-Specific Isotope Analysis (CSIA) to you Field Pilot Test*, Dec. 7, 2022

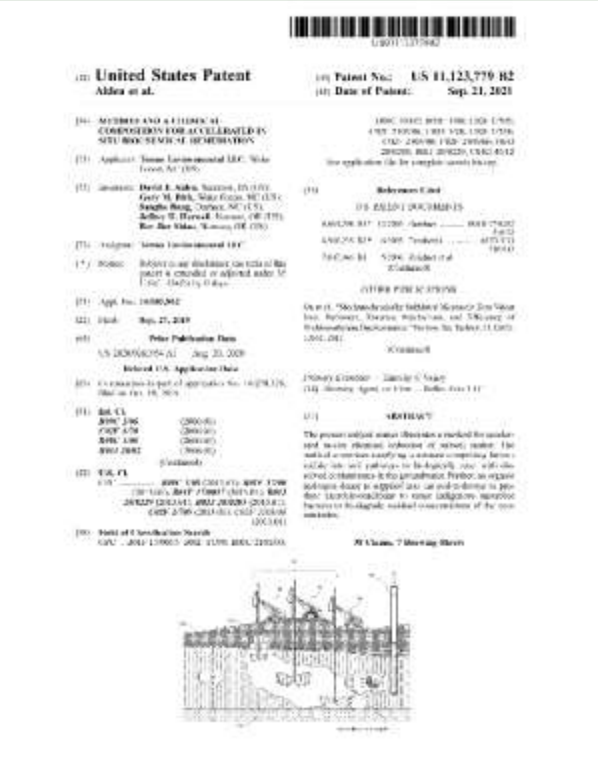
# Advantages

## Catalyzed Enhanced Reductive Bioremediation

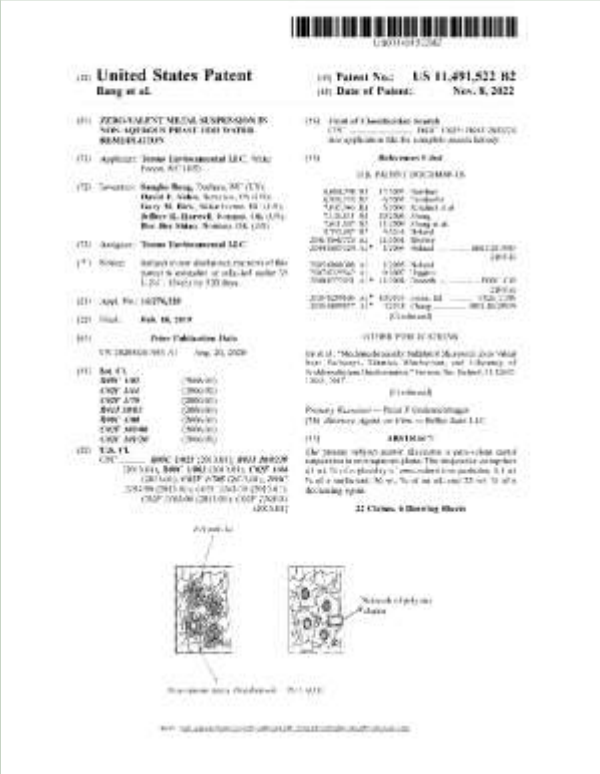
- Improved subsurface distribution of a vegetable oil-based electron donor
- Improved ROI, fatty acid distribution and TOC when compared to EVO
- Eliminates dependence on EVO droplet size
- Aids in reducing cVOC inhibitory concentrations by sequestering DNAPL
- High alcohol content and high solubility reduces injection well biofouling risk

# Abiotic Enhancement Options

## Zero-Valent Metal Particle Suspension Patents



United States Patent
Alden et al.
Patent No.: US 11,123,779 B2
Date of Patent: Sep. 21, 2021



United States Patent
Bang et al.
Patent No.: US 11,491,522 B2
Date of Patent: Nov. 8, 2022

# ZVI in Water vs iron-Gel™

# Iron Sulfide Reagent

## Provides

- Benefits of sulfidated ZVI
- Higher contaminant removal efficacy
- Lower cost

## Specifications

- Physical form:  colloidal suspension
- Specific gravity:  1.15 - 1.22
- ORP: -700 to -1300 mV

# Thermal Enhancement Options

## Apply Heat

- Enhances transesterification reaction
- Reduces time from days to months to minutes to hours
- 6 minutes
  - ✓ 90°C – 94% yield
  - ✓ 32°C – 64% yield

## Optimum Growth Temperature

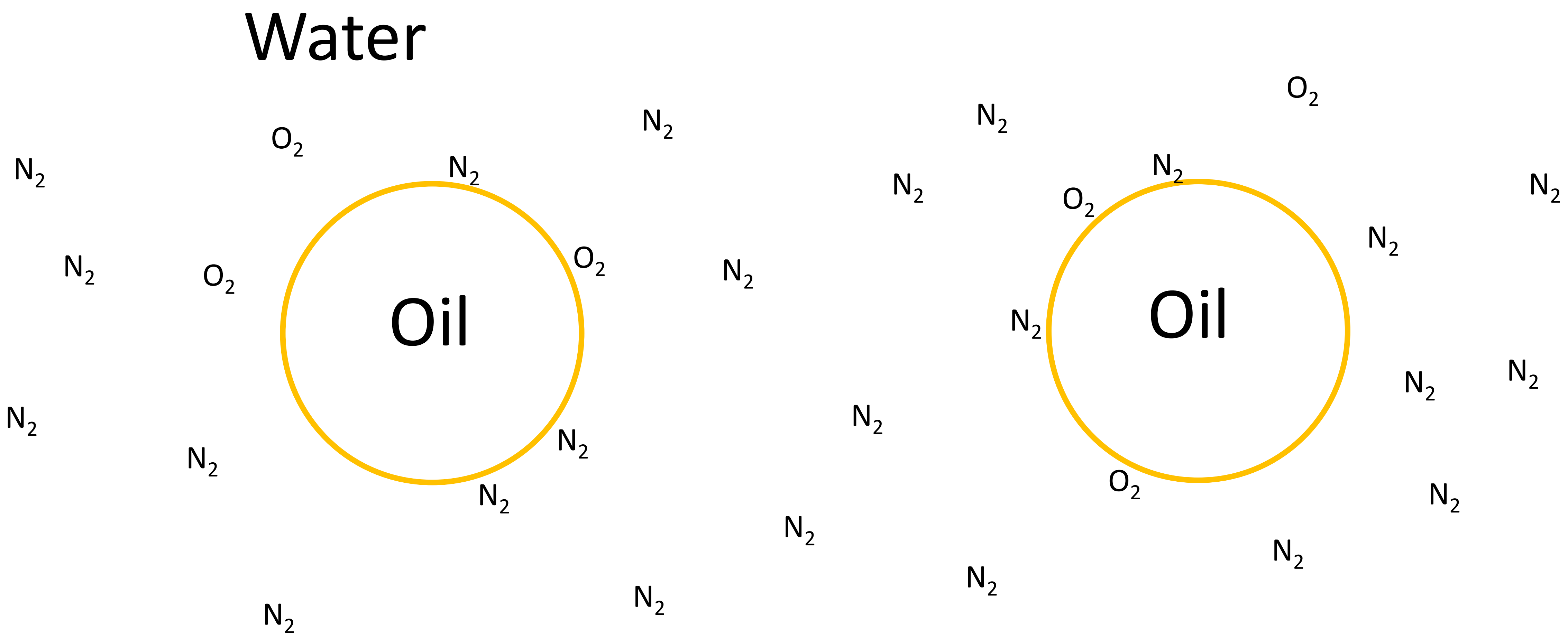
- 25-30°C hydrogenotrophic Dhc strains (Löffler et al., 2013)
- <40−45°C biotic or abiotic destruction
- > 50°C very little biotic or abiotic destruction (Stroo et al., 2013; Costanza et al., 2009)

# Hot water vs cold water

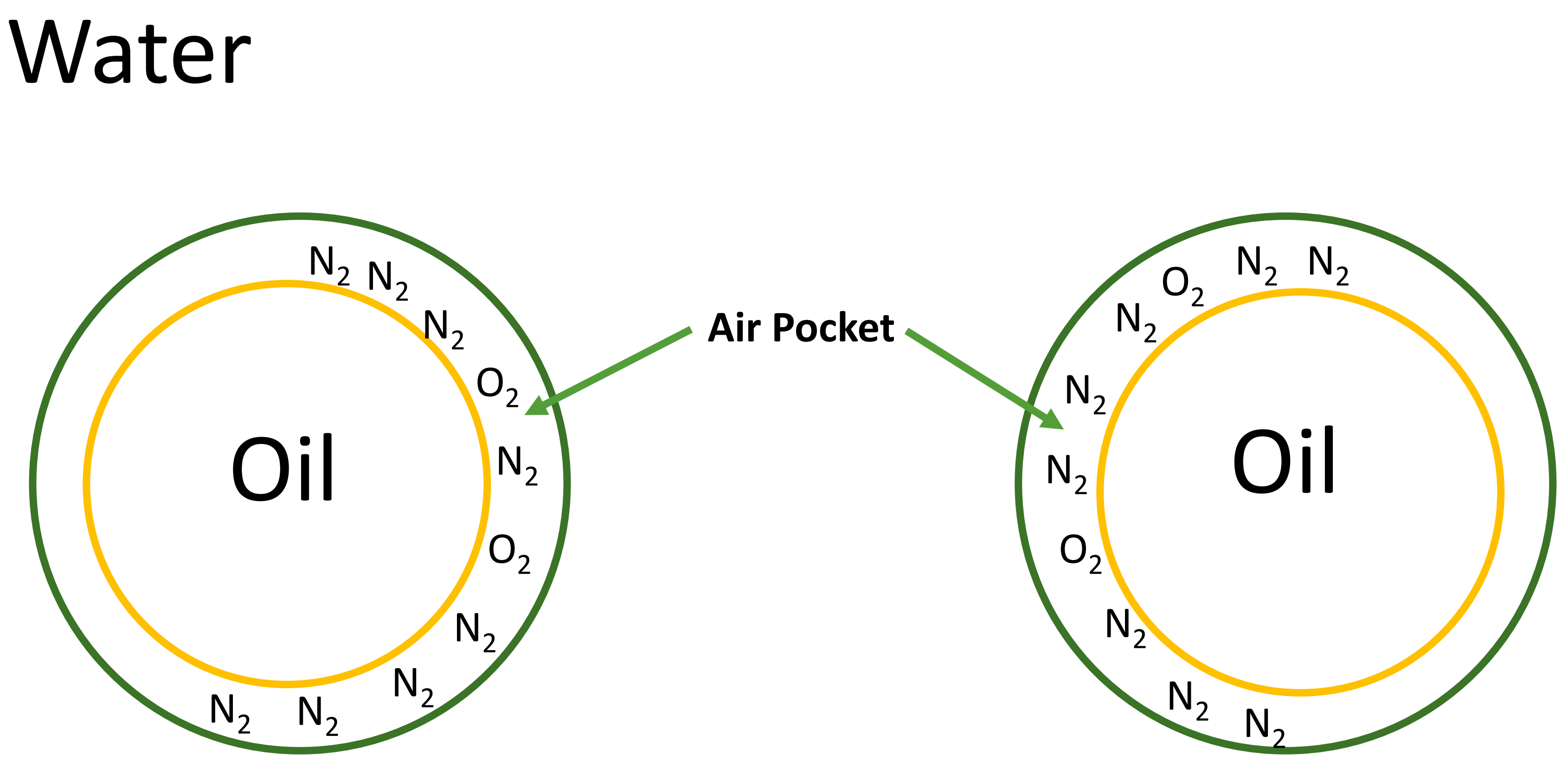
- Hot water dissolves fewer gases (e.g., oxygen or carbon dioxide)

- Hot water dissolves more solids (e.g., sugars)

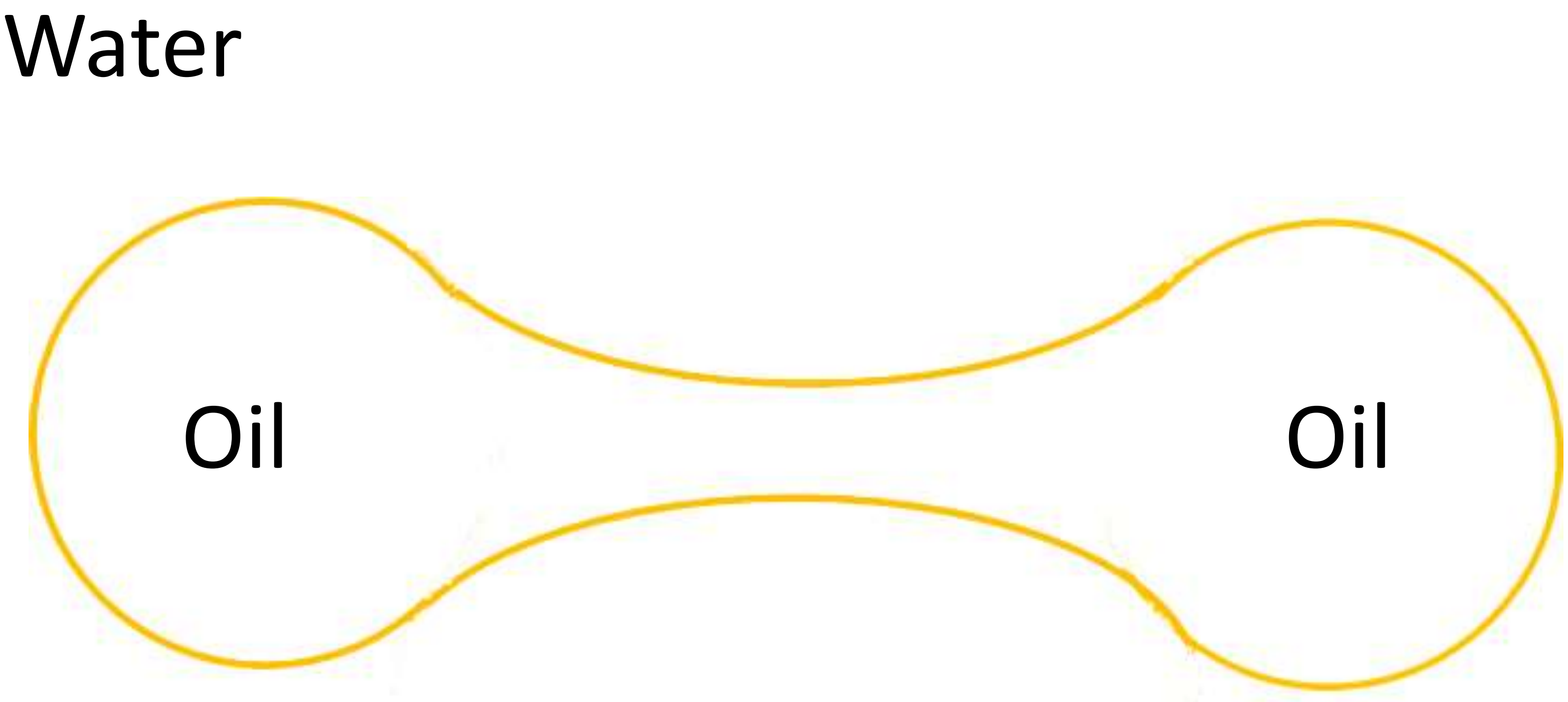
# Example of dissolved gas in water with oil



# The dissolved gas adsorbs to the surface of the oil

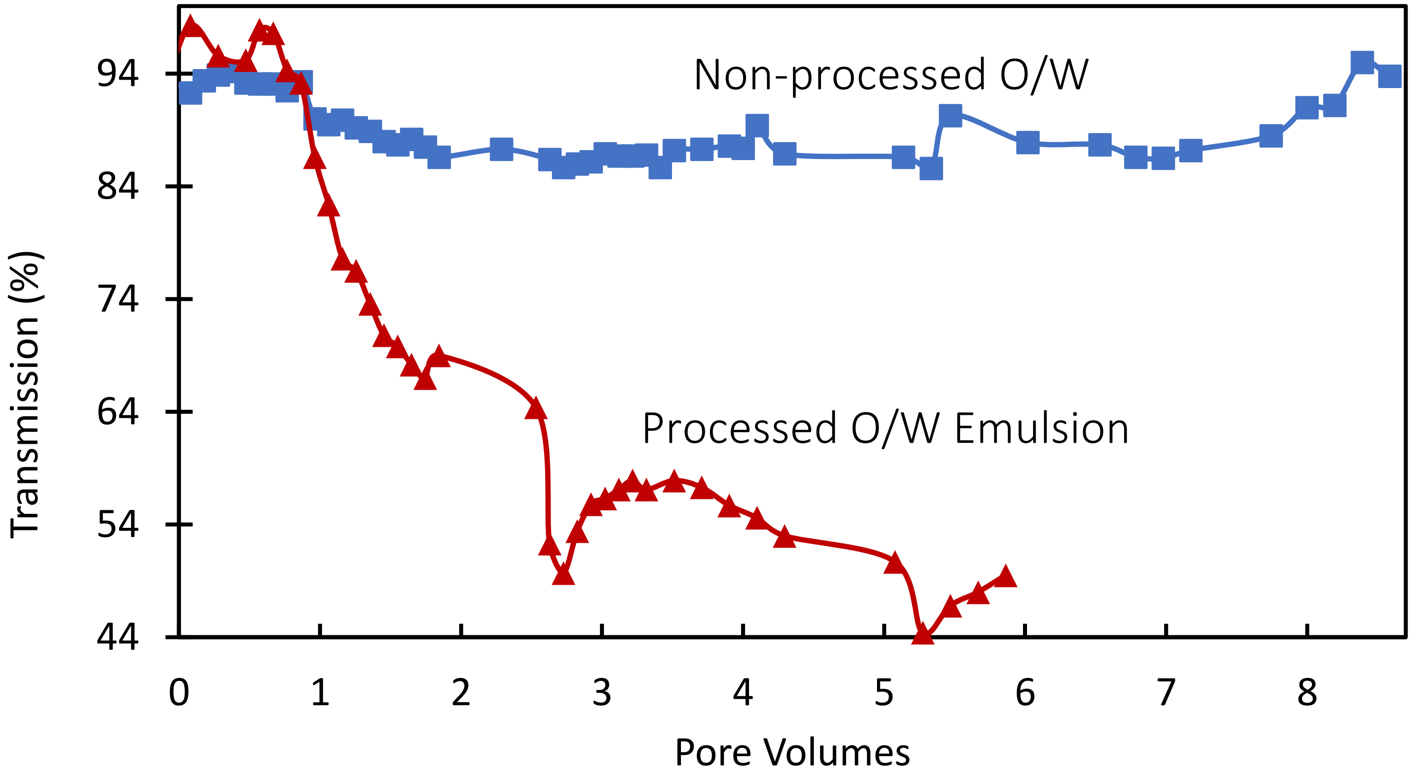


# Surface tension pushes oil droplets together to form one big droplet



# Processed Emulsions Remain Stable in Flow Through Porous Media

Photo of processed O/W emulsion after 1 hour



# Heating Options

**Conventional**

- Residual heat from an *in situ* thermal remediation project
- Electrical resistance heating
- Thermal conduction heating

**Heat amendments / water and inject**

- Hot water boiler
- Shell and tube heating tank or a batch heating tank with coils
- Solar collector, thermal storage tank with a submerged heat exchanger and an auxiliary heat exchanger

# Hot Water Injection

**Hydrogeological parameters**

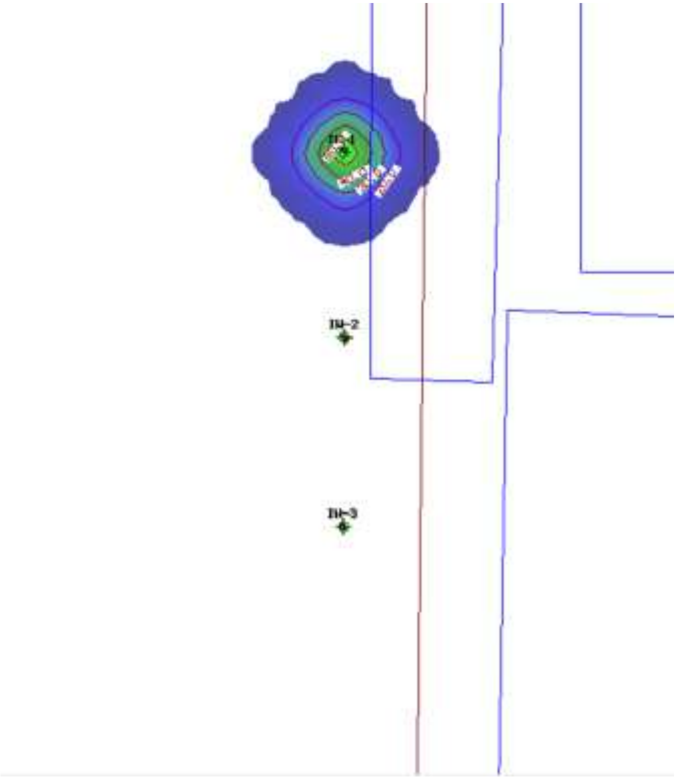
- Site lithology: sand
- Porosity: 0.33
- Aquifer hydraulic conductivity K of 1x10-2 cm/s
- Hydraulic gradient: 0.002 feet/feet

**Injection**

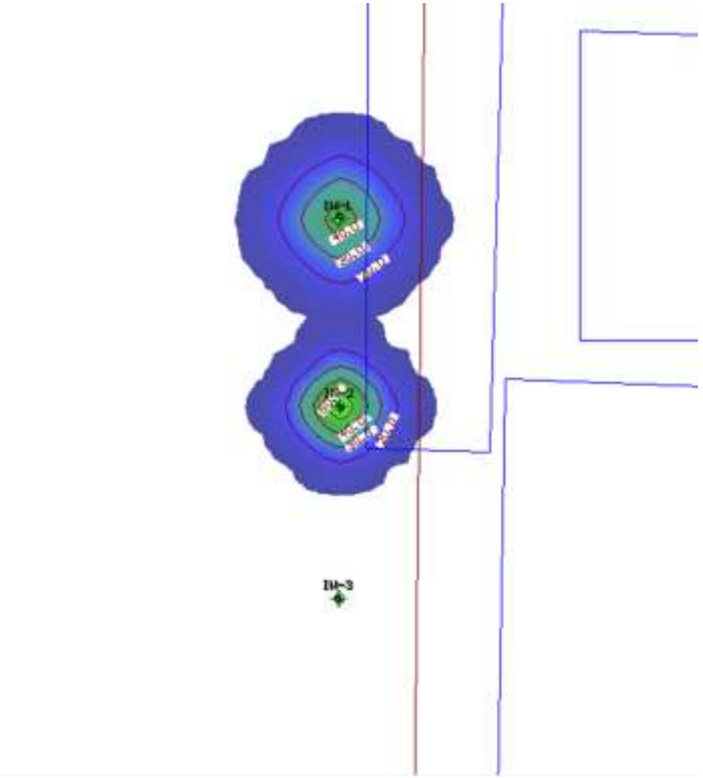
- 12-hour injection event
- 75 $m^3$ (19,813 gallons) of water heated to 90°C
- 150 $m^3$/d (27.5 gpm) flow rate

# Model Results

**Time = 0.5 days**

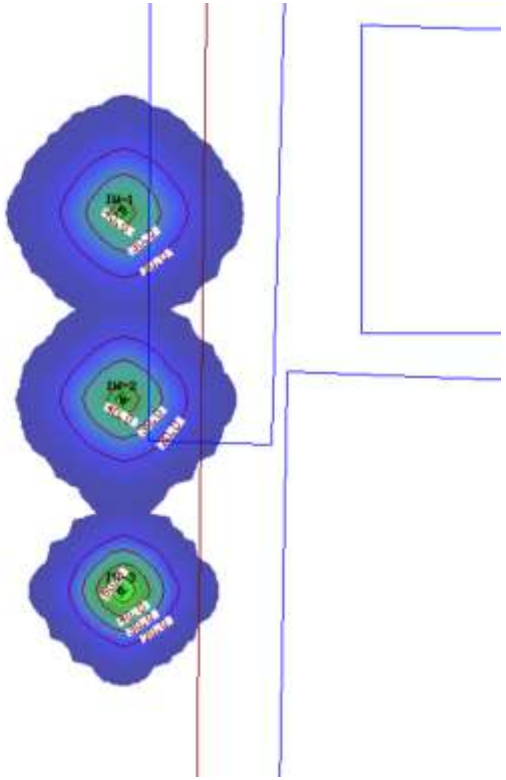


**Time = 1 day**

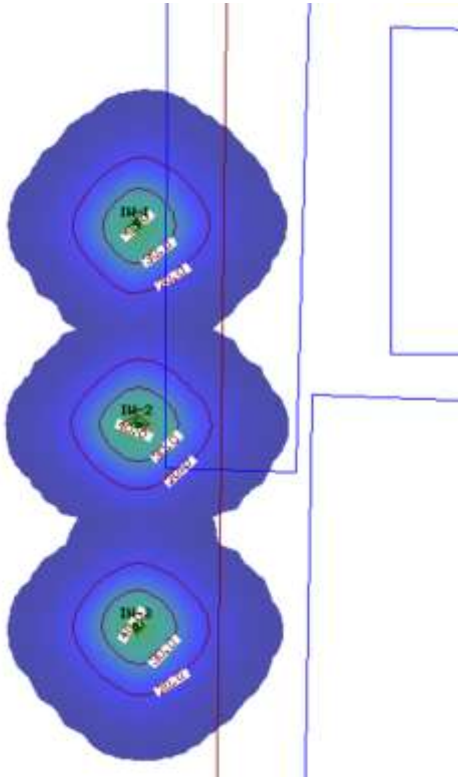


# Model Results (continued)

## Time = 1.5 days

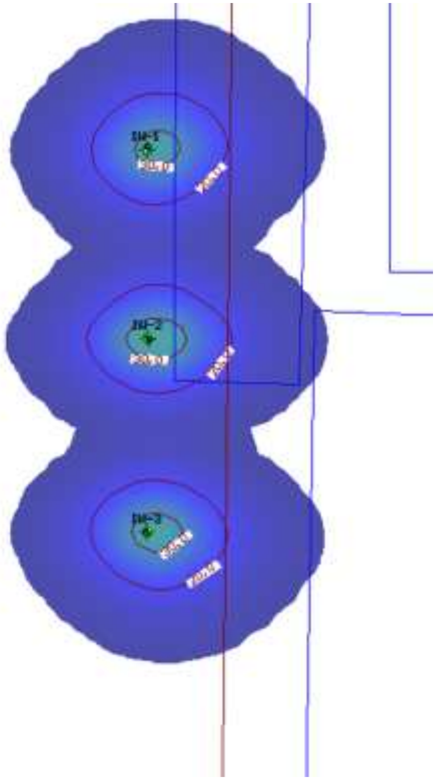


## Time = 5 days

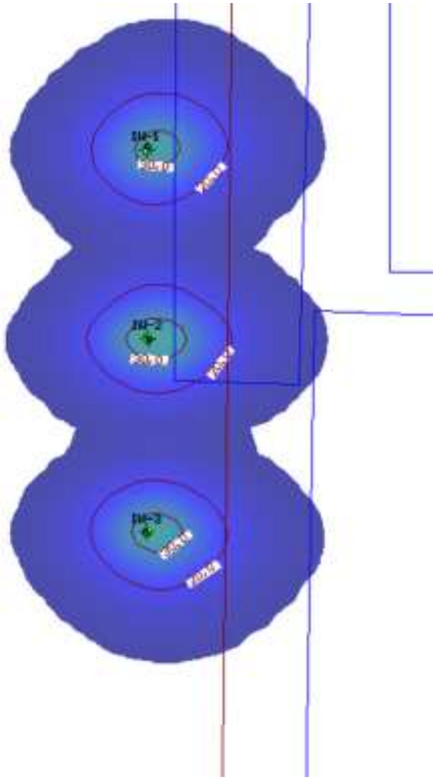


# Model Results (continued)

**Time = 10 days**

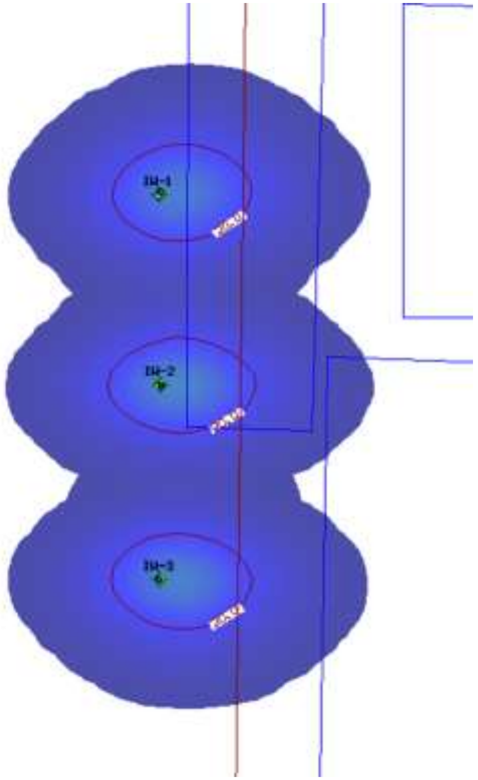


**Time = 30 days**

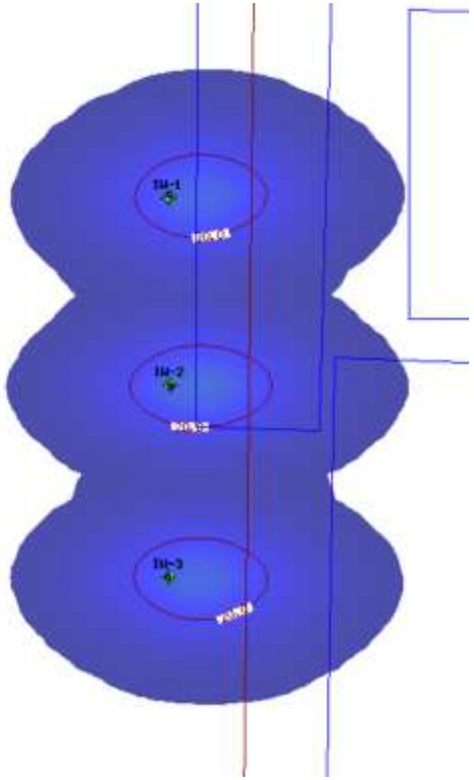


# Model Results (continued)

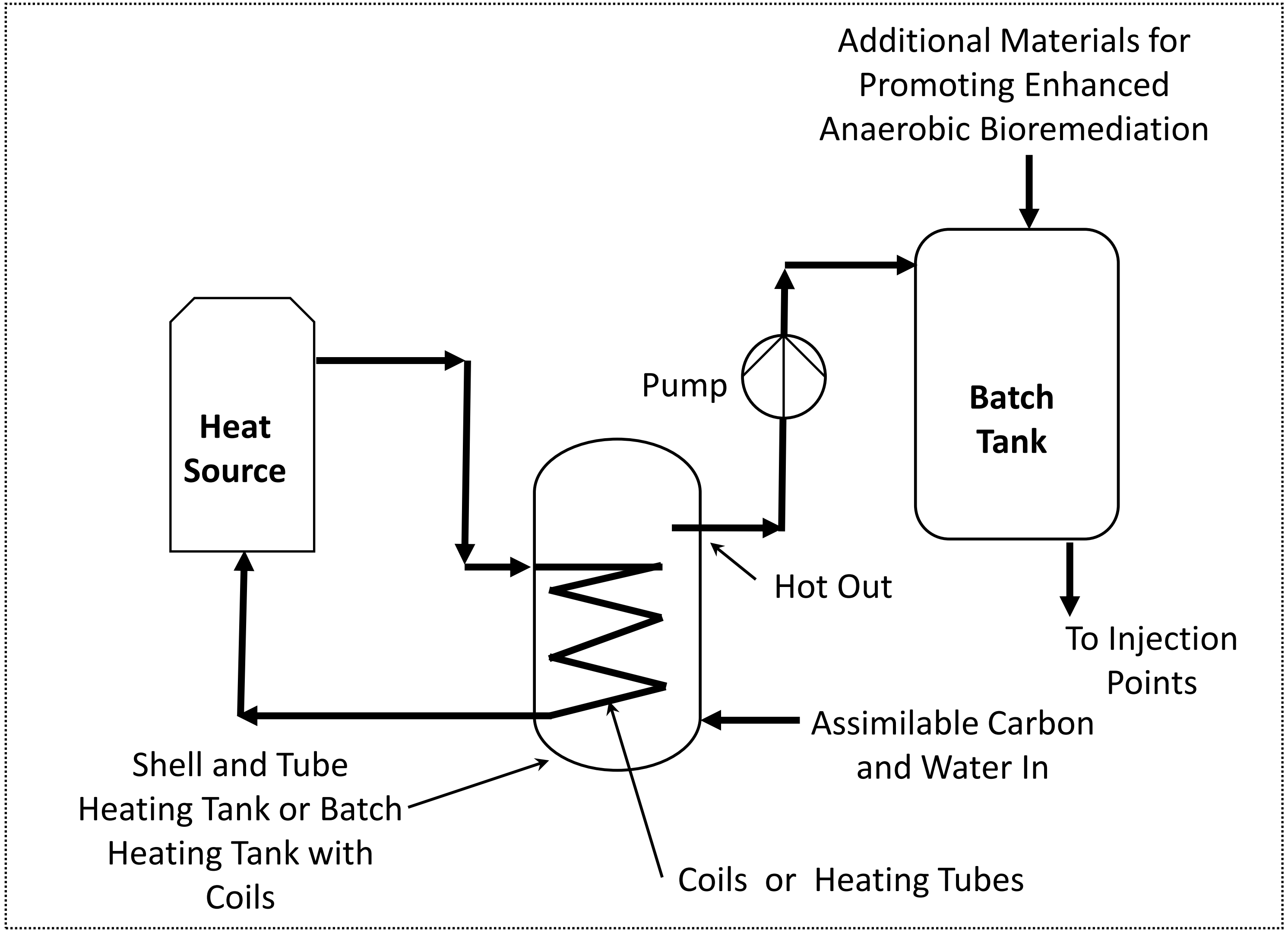
**Time = 60 days**



**Time = 90 days**



# Shell and Tube Heating Tank or Batch Heating Tank with Coils




Photograph Curtesy of Corporativo SIRN S de RL de CV

# Tankless Heaters


| Water Heating Capacity Data | |
|---|---|
| Temperature Rise (°F) | Flow Rate (GPM) |
| 35 | 12.1 |
| 45 | 9.4 |
| 55 | 7.7 |
| 65 | 6.5 |
| 75 | 5.6 |
| 90 | 4.7 |
| 100 | 4.2 |
| 120 | 3.5 |
| 140 | 3.0 |

Potential Reaction Temp of 30 to 40°C (rows 65 to 100)

# Heat Enhanced Reductive Bioremediation

- Microbes that do all the work like a warm environment

- Warm water has lower dissolved gases

- Heating increases transesterification reaction rates

# Thank you

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