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Two in situ remediation innovations: for treating high contaminant concentrations

Gareth Leonard
Intersol 2019

Sulfidated Micro-scale Colloidal Zero Valent Iron

Engineered Zero Valent Iron product:

- Colloidal – particle size <5µm
- Sulfidated particle coating
- Glycerol suspension

This combination results in:

- Abiotic degradation
- ISCR enhanced biological degradation

Targeting:

- Chlorinated solvents – PCE, TCE, TCA
- Pesticides

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S-Micro ZVI™
Sulfidated Zero-Valent Iron

What are we trying to improve upon?

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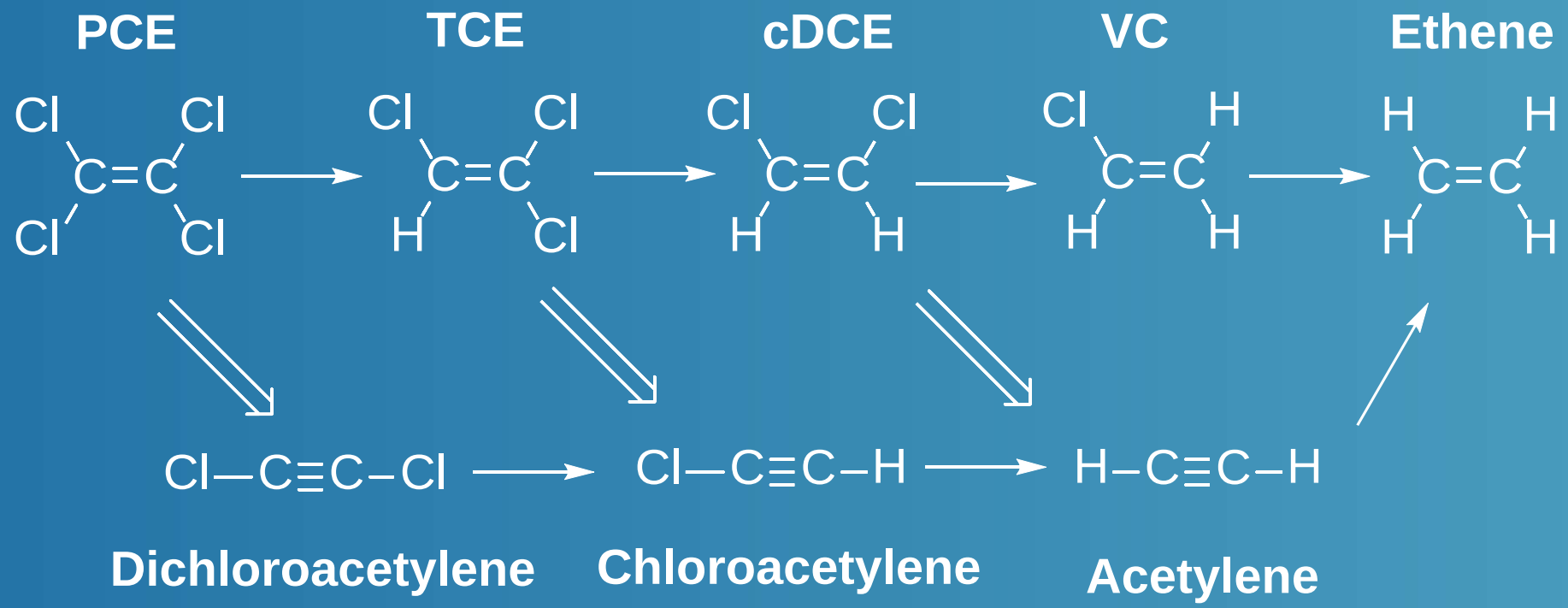
1) REACTIVITY: Two processes

Biotic: Enhanced Reductive Dechlorination

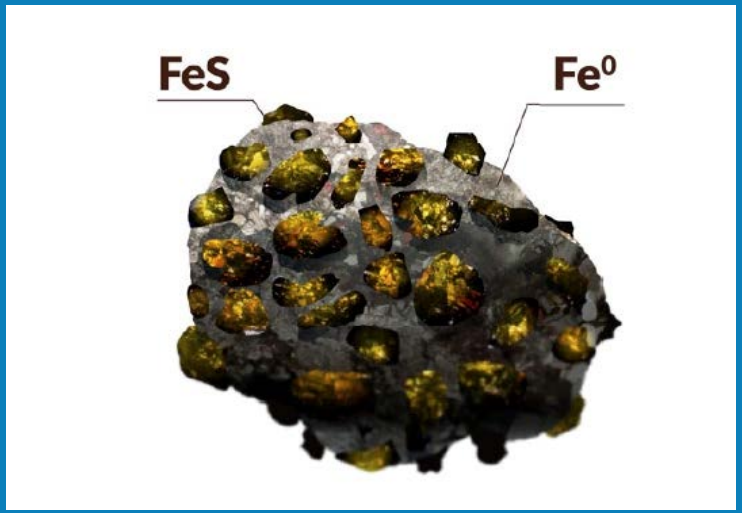


Abiotic: Reaction pathway can bypass toxic daughter products

1) Reactivity - Sulfidation

ZVI also reacts with water = H_2

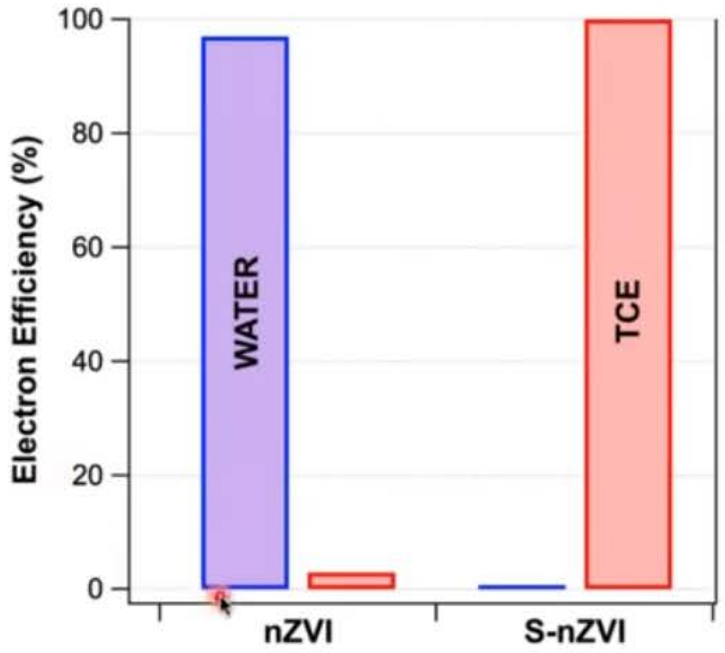
- Results in:
  - passivation
  - decreased persistence
  - Less treatment of the contaminant



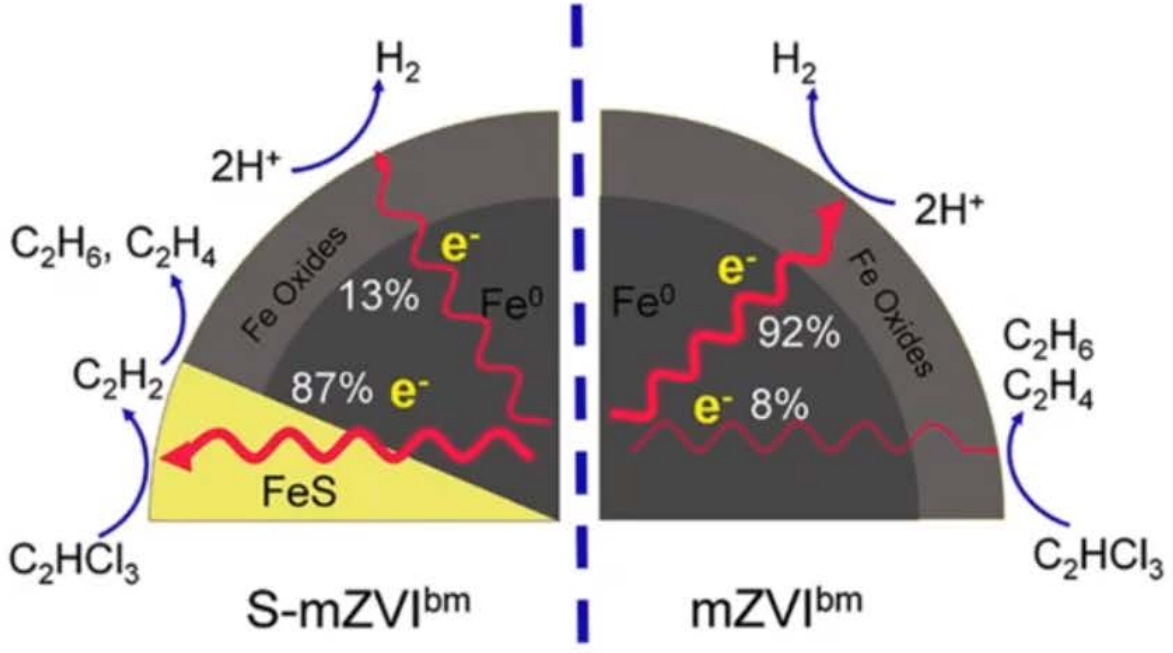
Answer = sulfidate the ZVI surface

- Coats the surface of the ZVI particle with iron sulfide
- Results in an increase in Electron Efficiency (EE):
  - Minimizes reaction rate with water
  - Maximizes reaction rate with contaminants
- Sulfidation enhances reaction rate with chlorinated ethenes

1) Reactivity - Sulfidation



Fan, O'Brien, et al. (2016)
Env. Sci. Technol. 50: 9558-9565
Sulfidation of nZVI for Improved Selectivity during ISCR



Gu, Wang, He, et al. (2017)
Env. Sci. Technol. 51: 12653-12662
Mechanochemically Sulfidated mZVI: Pathways, Kinetics, Mechanisms, Selectivity

From Dr Paul Tratnyek, Oregon Health and Science University

2) DISTRIBUTION: COLLOIDAL ZVI SUSPENSIONS

SMALL PARTICLE SIZE ZVI

LARGE PARTICLE SIZE ZVI

<5 micron S-MicroZVI in water

40 micron ZVI in water

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2) DISTRIBUTION: Mixing and Injection

Characteristics of colloidal iron

S-MicroZVI suspension

Low pressure sandbox demo

Characteristics of microscale iron

Microscale ZVI Slurry

Depiction of subsurface fractures

3) EASE OF USE

- A fluid suspension is provided in 200L drums
- Pumped or poured into mix tank and diluted
- Simple mixing and pumping equipment
- Safe to use

- No need for powder handling equipment
- No dust or explosion hazard
- No thick slurries to fracture into the formation

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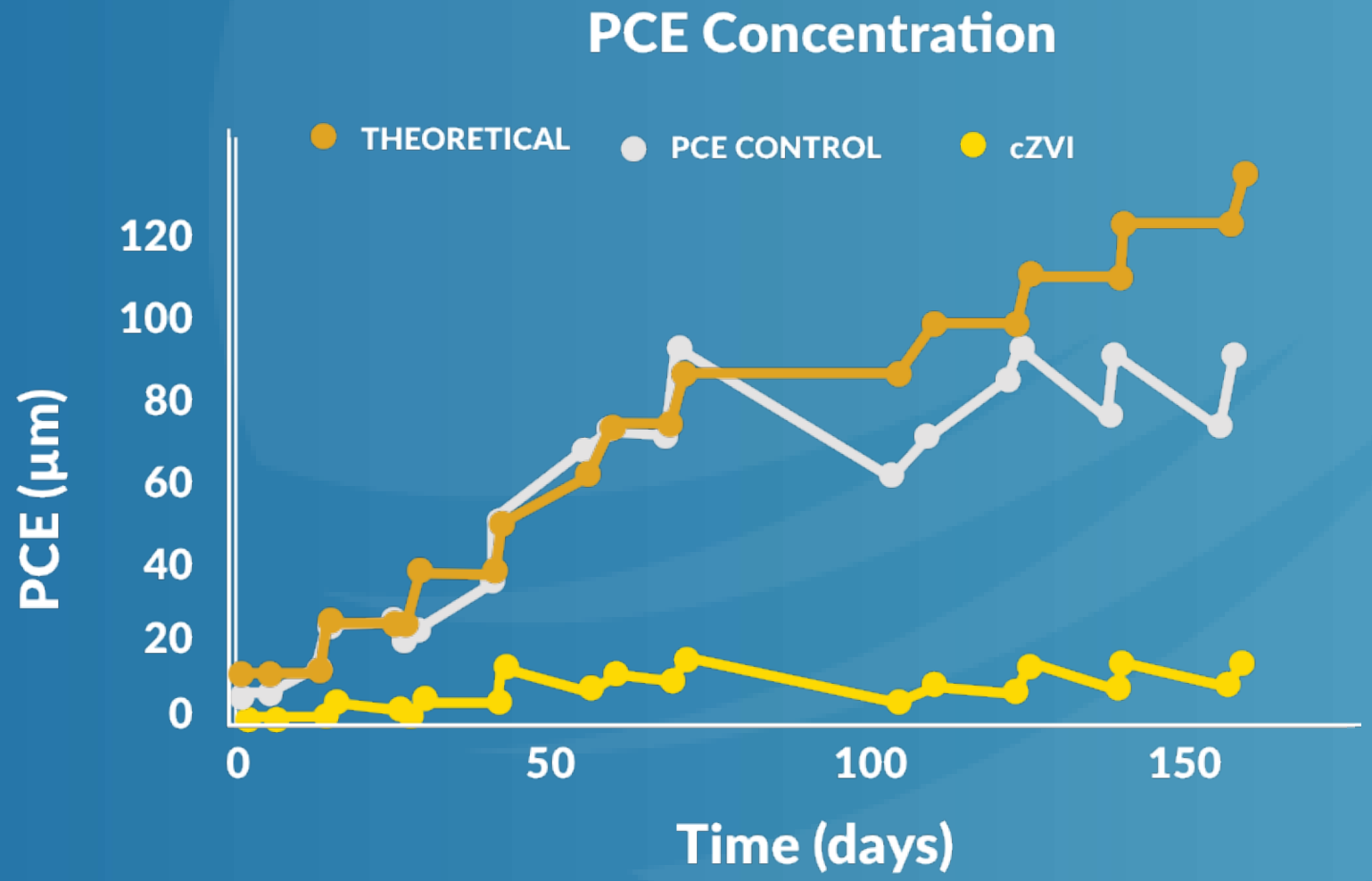
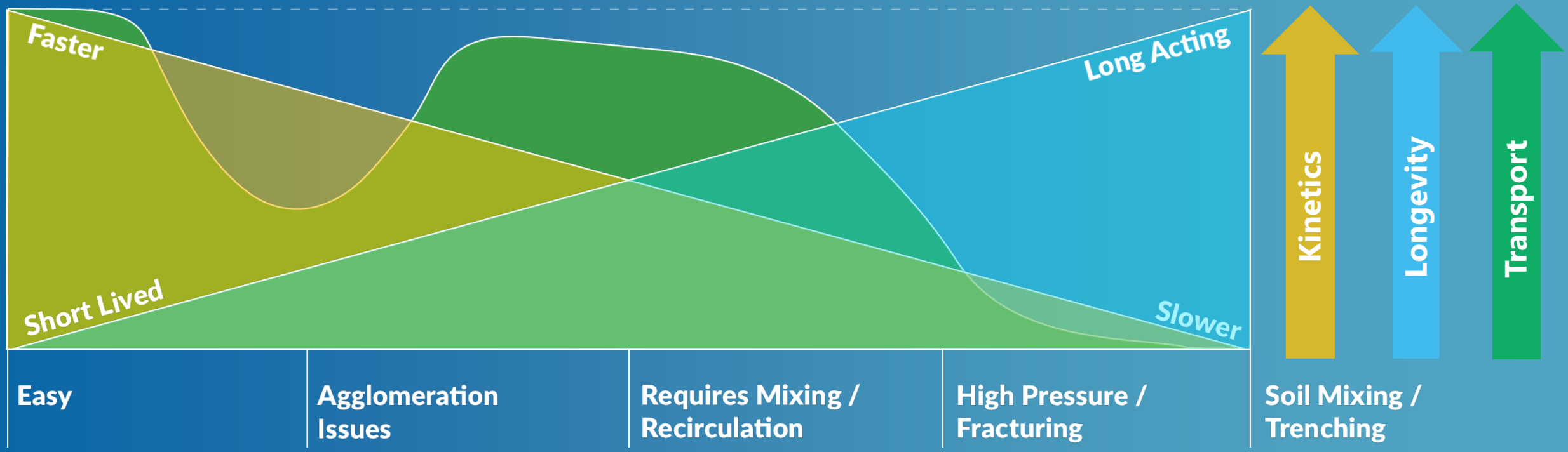
4) Persistence

- Improved EE from sulfidation
- Reduction in passivation



FEATUES OF DIFFERENT PARTICLE SIZE ZVI

Soluble	Nano	Near-Microscale	Far-Microscale	Scrap Iron
Fe^{+2}	NZVI	Colloidal ZVI	Powdered ZVI	
0 µm	0.2 µm	1-4 µm	50 µm	1 mm



Easy	Agglomeration Issues	Requires Mixing / Recirculation	High Pressure / Fracturing	Soil Mixing / Trenching

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S-Micro ZVI™
Sulfidated Zero-Valent Iron

Sulfidated Micro-scale Colloidal Zero Valent Iron

- Reduction in daughter products
- Excellent distribution
- Easy to use
- Enhanced reactivity with contaminants (10-30x that of commodity ZVI)
- Enhanced persistence
- Can target high concentrations of contaminants
- Integrates with electron donor substrates

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S-Micro ZVI™
Sulfidated Zero-Valent Iron

Dual Function Activated Carbon Amendment

- Consists of:

1. micro scale activated carbon particles (<1-2 µm) and slow release sulphate electron acceptor
2. Nitrate and sulphate electron acceptor mix

- Provides a combination of:

1. Rapid sorption of mobile contamination
2. Facilitates the onset of natural biological degradation

- Targets contaminant:
  - Petroleum hydrocarbons
  - BTEX, TPH-G, TPH-D, MTBE, naphthalene, etc

Application

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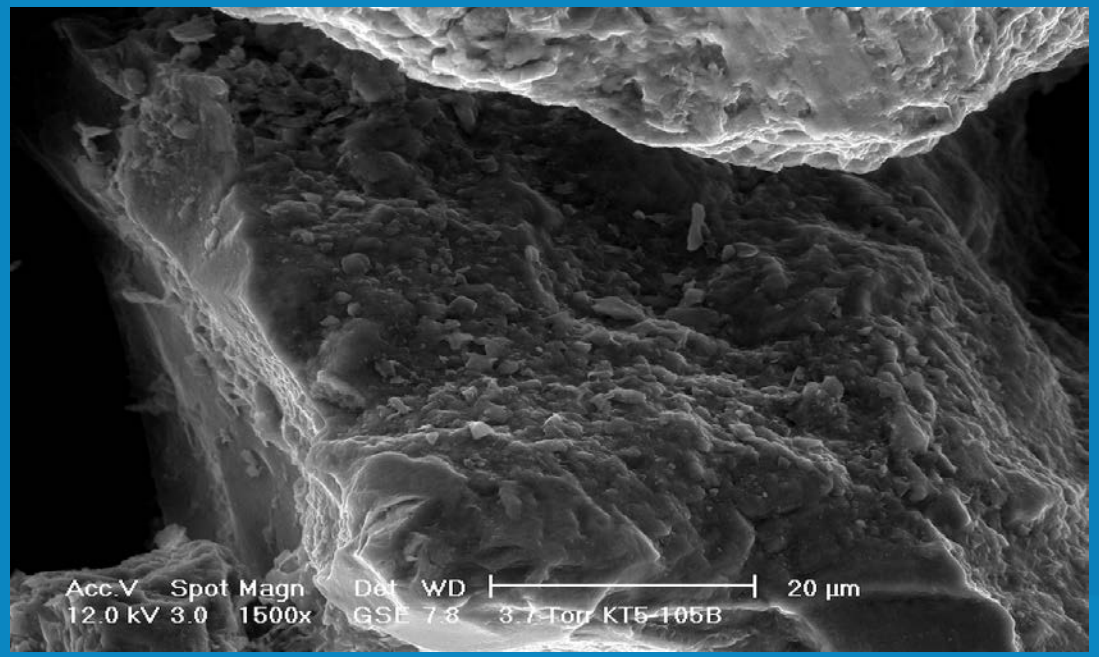
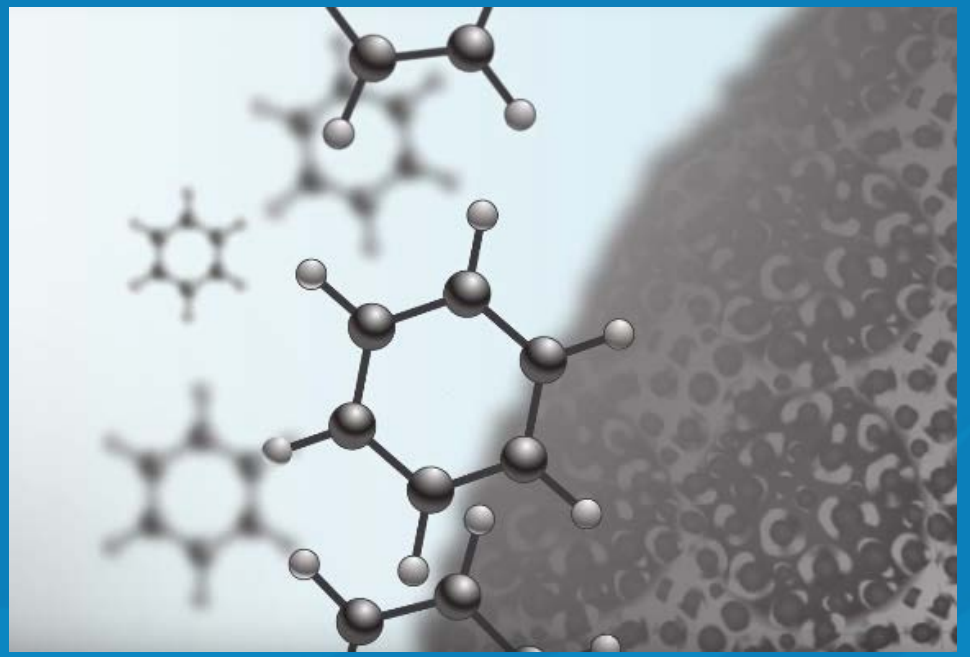
Photos from Rake Remediation and Tergeo Consulting

Remediation Process

1) Adsorb contaminants onto activated carbon





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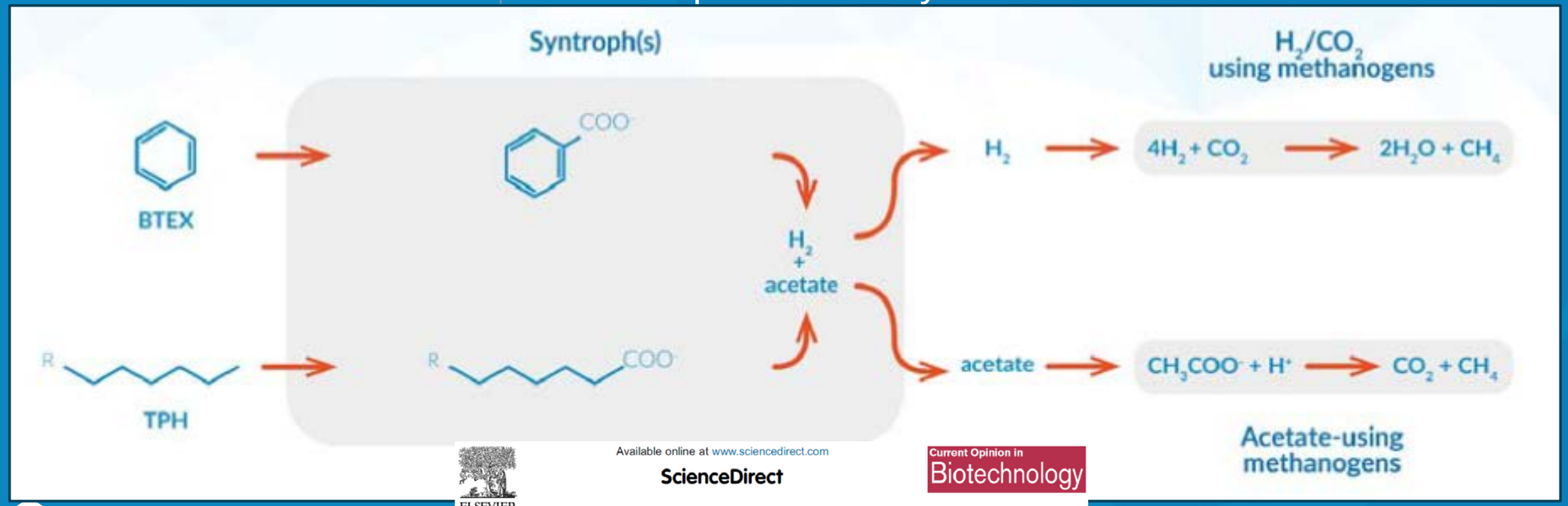
Remediation Process

2) Provide initial biological degradation using NO_3^- and SO_4^{-2}
   - Anaerobic biological degradation
   - Stimulate syntrophic conditions to sustain biodegradation to expedite the natural attenuation of residual petroleum hydrocarbons



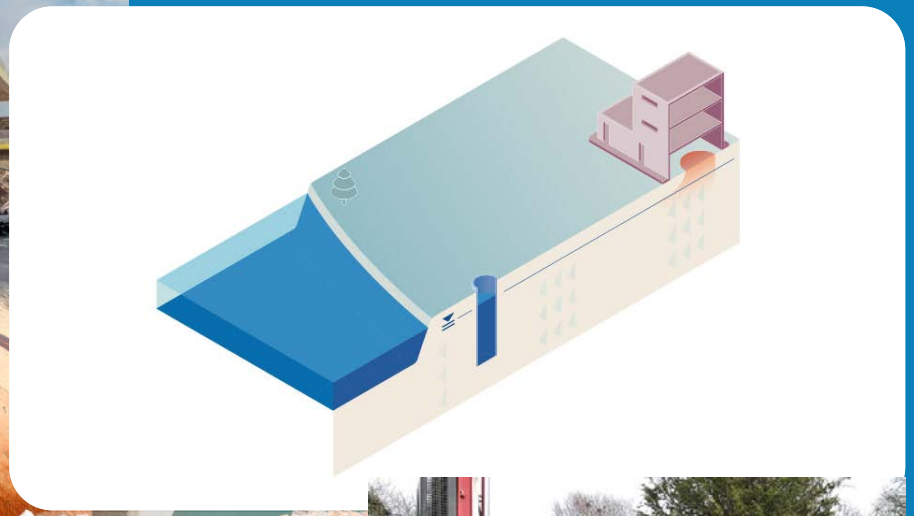
Available online at www.sciencedirect.com
ScienceDirect
Current Opinion in Biotechnology
ELSEVIER

Syntrophic biodegradation of hydrocarbon contaminants

Lisa M Gieg, S Jane Fowler and Carolina Berdugo-Clavijo

Application scenarios

1. **Petrol Filling Stations**
    1. Tank replacement
        - Excavation application
    2. Barrier treatment
    3. Legacy sites
        - Liability reduction
2. **Oil Spills**
    - Excavation application or injection
    - Tankers/Broken pipes
    - Reduce extent of impact
3. **Vadose Zone**
    - Prevent mobilisation/desorption during infiltration or groundwater fluctuation
4. **Preventative Measure**
    - Application into UST or pipe bedding
5. **Integrated**
    - Barrier near source, polishing step



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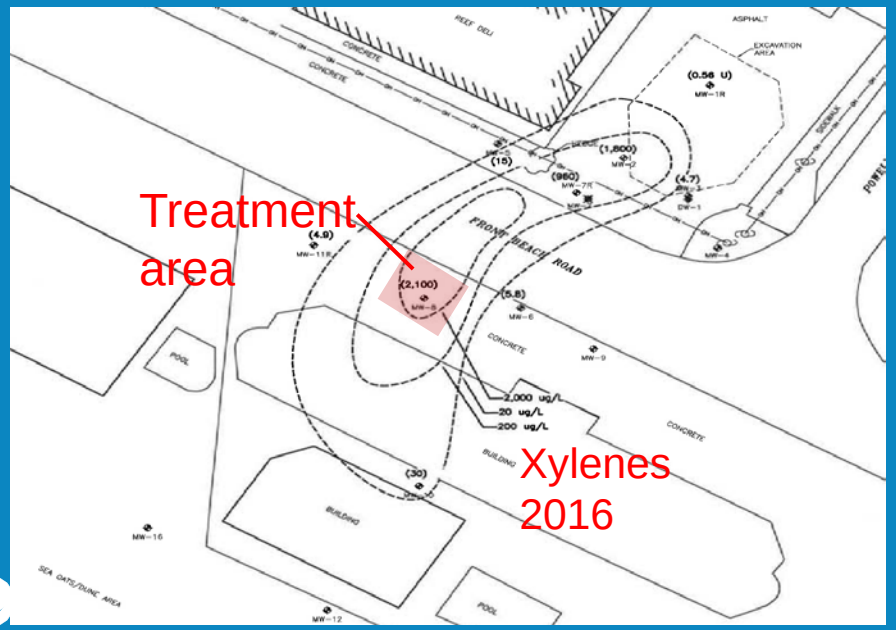
Beta Site Performance Review

Site 1 - Panama City Beach, Florida

- Very fine, homogeneous sand
- 10 direct push points
- 770 kg of PetroFix injected
- BTEX+Napth – 1,300 to 14,300 ug/l, TPH 4,300-15,000 ug/l since Feb



Chemical data

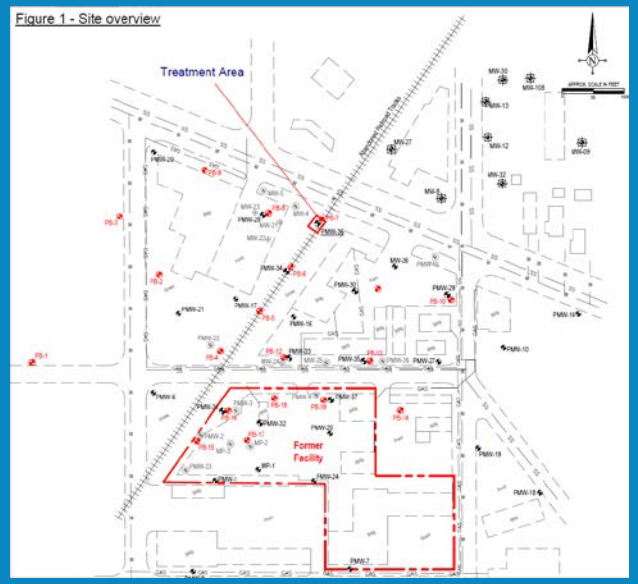
(units µg/L)	Mar 2018	May 2018	June 2018	Sept 2018	Dec 2018
Benzene	1.5	ND	ND	ND	ND
Toluene	ND	ND	ND	ND	0.3 J
Ethylbenzene	270	ND	ND	ND	ND
Xylenes	860	ND	ND	ND	ND
TPH-GRO	3,100	ND	ND	ND	ND

Full-scale application in Spring 2019

Beta Site Performance Review

Site 2 - South Bend, Indiana

- Heterogenous soils
- 12 direct push points
- 900 kg of PetroFix injected
- BTEX – 3,500 ug/l, TPH-G –38,800 ug/l, TPH-D –17,800 ug/l



(units µg/L)	May 2018	Jun 2018	Aug 2018	Nov 2018	Feb 2019
Benzene	149	ND	ND	ND	69.9
Toluene	191	ND	5.7	ND	139
Ethylbenzene	330	ND	5.6	14	49.1
Xylenes	2,610	ND	30	ND	181
TPH-GRO	33,800	ND	ND	ND	1,170
TPH-DRO	17,800	3,600	4,200	250	596

Full-scale application in May 2019

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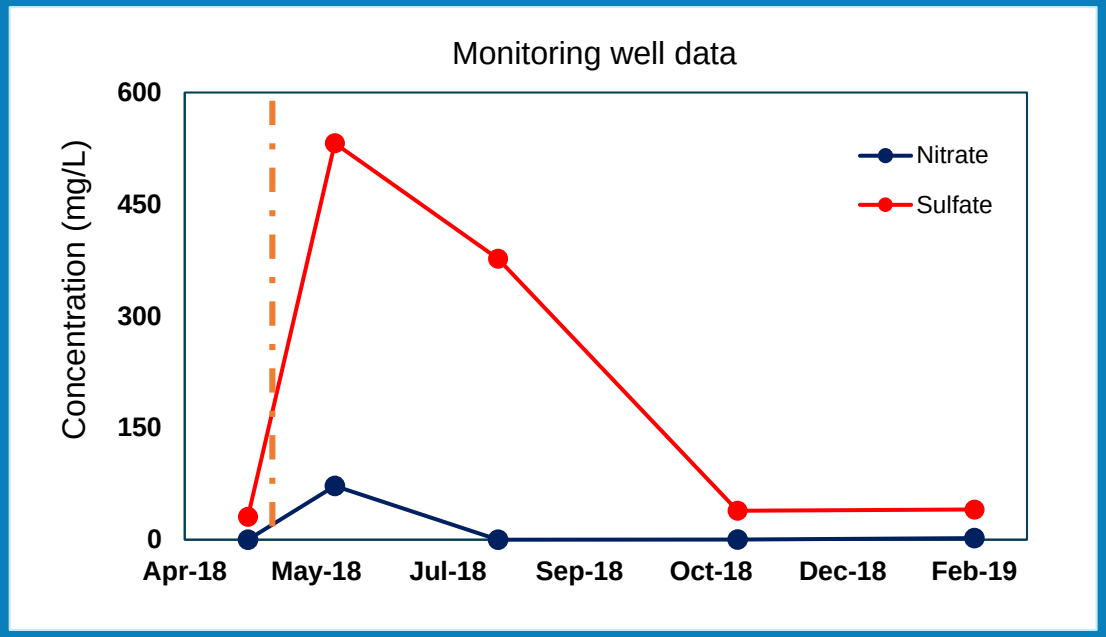
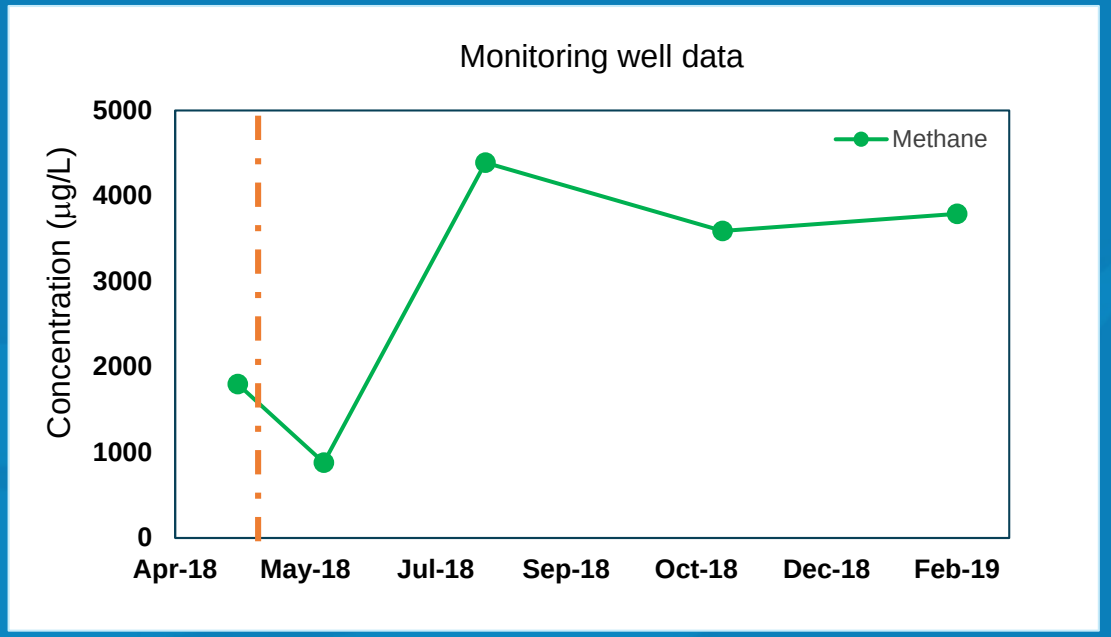
Beta Site Performance Review

Site 2 - South Bend, Indiana

- As expected nitrate used first, followed by sulfate
- Increased methane production (from PHC biodegradation) lasting after nitrate, sulfate consumed





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Thank you

Any questions?

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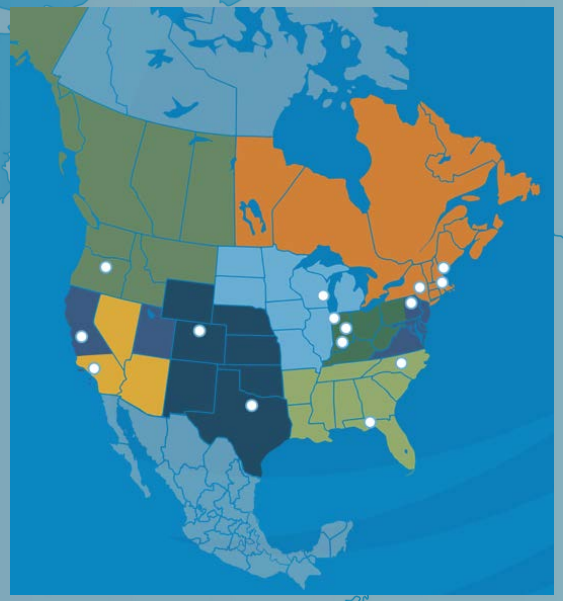

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