Optimization of ZVI Technology for *In-Situ* Remediation of Chlorinated Contaminants

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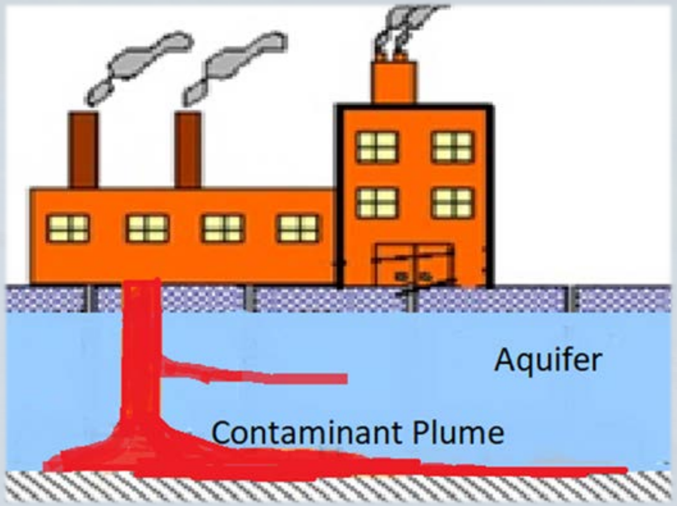
EST. 1992

Chlorinated Solvent Contamination - Background

- **Dry cleaners**
  - PCE used as cleaning agent
  - Many dry cleaning facilities had leaks, spills, improper disposal
- **Former and current industrial facilities**
  - PCE, TCE, VC, 1,1,1-TCA, etc.
  - Degreasing, cleaning, surface preparation
  - Remanufacturing, metalworking, etc.
  - Electronics manufacturing
- **Aerospace / defense installations**
  - Cleaning agents for planes, weapons, etc.
  - PCE, TCE, VC, 1,1,1-TCA, etc.



Primary contaminants and daughter products have varying levels of toxicity.

Chlorinated Solvent Contamination - Remedial Options

Physical Methods:

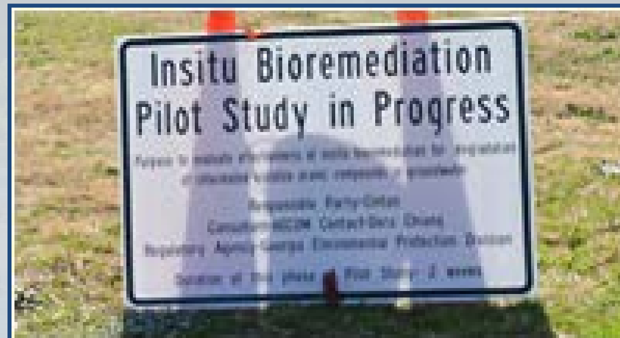
- Excavation - Soil Mixing - Soil Vapor Extraction

***In-Situ* Methods:**

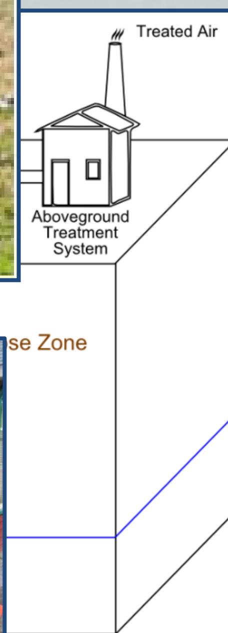
- Chemical Reduction - Bioremediation - Chemical Oxidation

Source: Geo-Solutions

Source: OnMaterials



Source: Terra Systems



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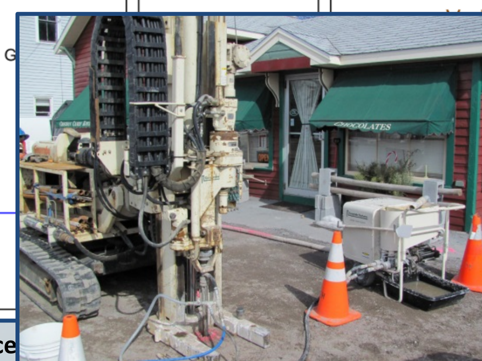


Source: NRC

Why use Zero Valent Iron?

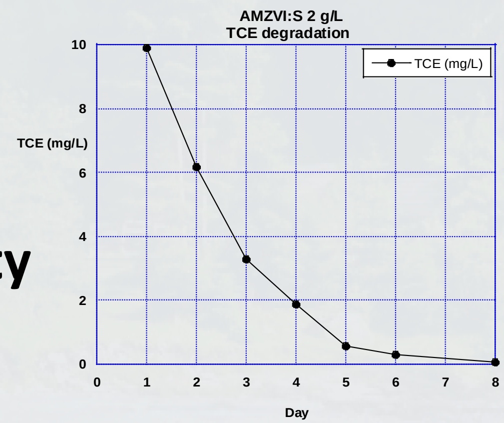
- If used properly, ZVI can address chlorinated contamination through either **chemical reduction** and/or **enhanced bioremediation** pathways.

- It is possible to use ZVI in a manner which satisfies all of the requirements for successful *in situ* remediation…

- *In-Situ* remediation technologies are attractive because they don't involve excavation or permanent system installation (O&M costs)

Requirements for Successful *In-Situ* Remediation

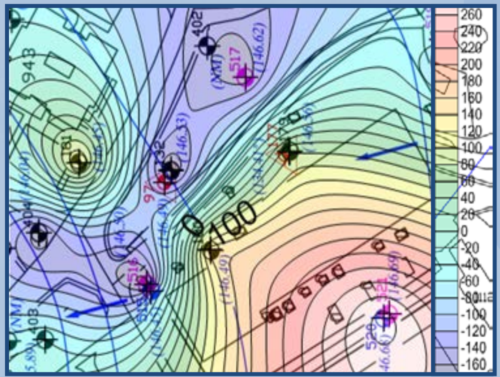
Reactivity



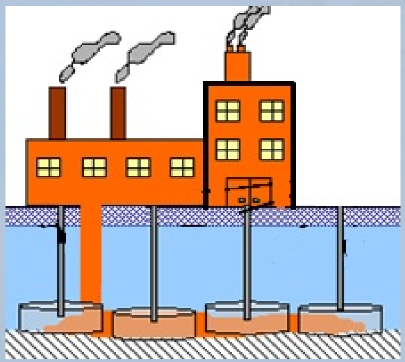
Ease of Use

Success!

Persistence

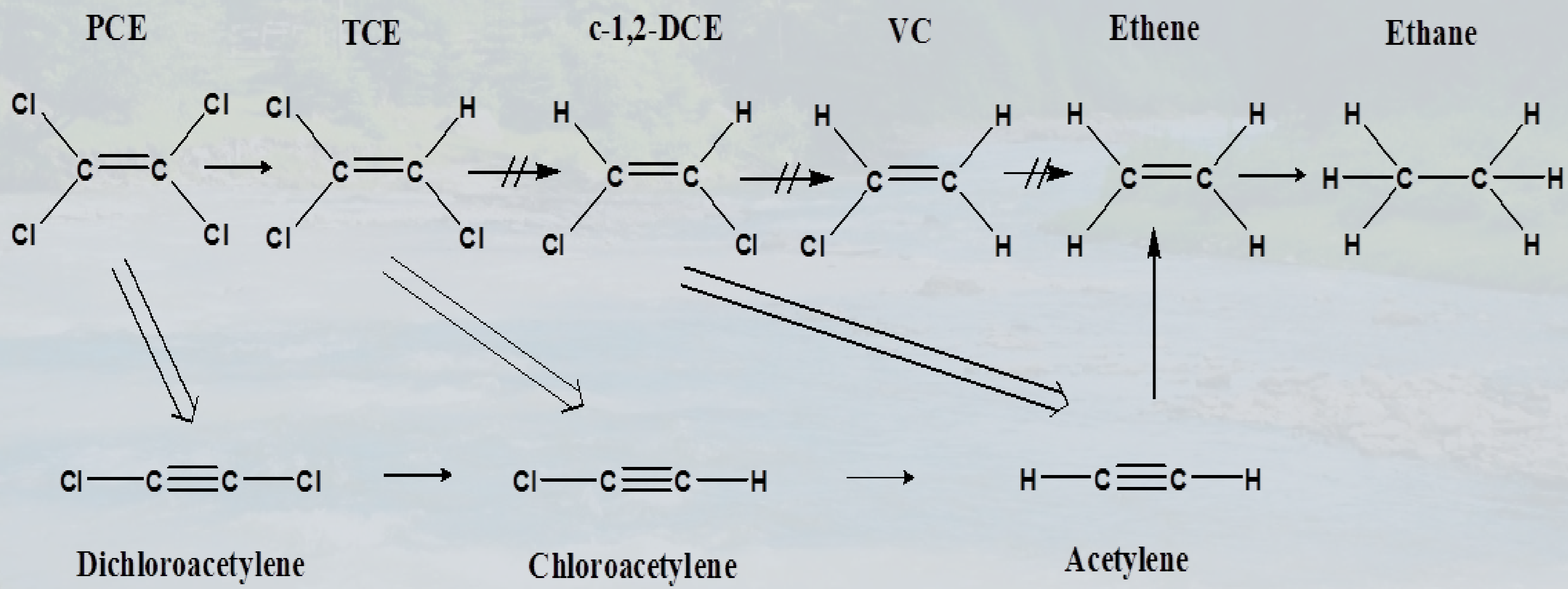


Distribution



Chemical Reduction (Abiotic): Zero Valent Iron and TCE

$$4Fe^0 + C_2HCl_3 + 5\,H^+ \rightarrow 4\,Fe^{+2} + C_2H_6 + 3\,Cl^-$$



Reaction pathway can bypass toxic daughter products

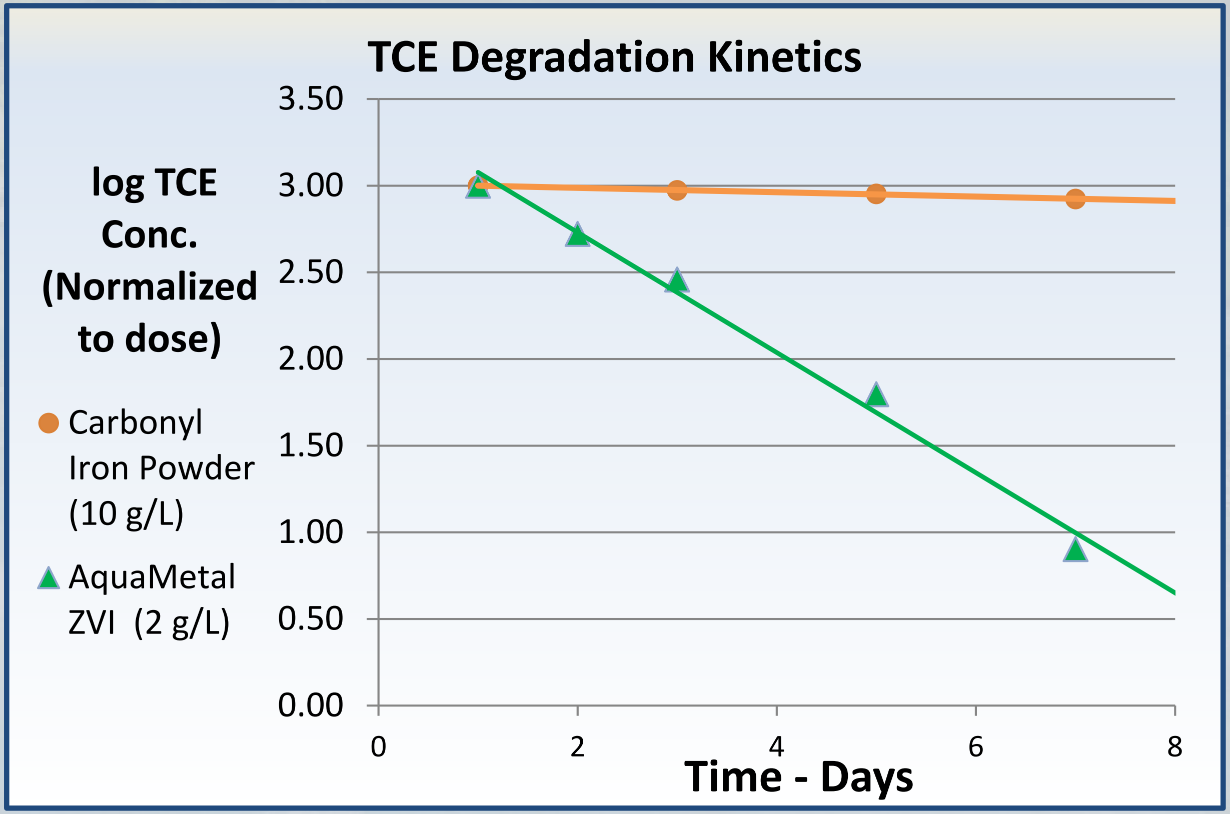
Reactivity: Commodity Iron Vs. Engineered Iron

Comparison of the following against 36 mg/L TCE:

- **10 g/L** Carbonyl iron powder (commodity product)
- **2 g/L** Z-Loy™ AquaMetal ZVI (engineered product)

Z-Loy™ AquaMetal ZVI exhibits a 27x faster degradation rate.

- Particle size reduction
- Increased reactive surface area
- Surface preparation & catalysis



ZVI – Passivity and the Importance of Optimized Material

Reaction with water

$Fe(s) + 2\ H_2O(l) \rightarrow \mathbf{Fe(OH)_2(s)} + H_2(aq)$

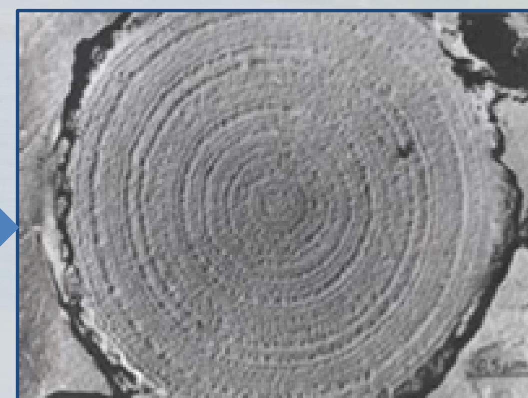
$3\ Fe(OH)_2(s) \rightarrow \mathbf{Fe_3O_4(s)} + H_2(aq) + 2H_2O(l) \rightarrow$ **Passivating oxide/ hydroxide**

Reaction with DO

$2\ Fe(s) + 1.5\ O_2(aq) \rightarrow \mathbf{Fe_2O_3(s)} \rightarrow$ **Passivating oxide**

Reaction with Carbonate

$Fe(s) + 2\ H_2O(l) + CO_3^{-2}(aq) \rightarrow \mathbf{FeCO_3(s)} + H_2(g) + 2\ OH^-(aq) \rightarrow$ **Passivating carbonate**



Reaction with Sulfate

$4\ Fe(s) + SO_4^{-2}(aq) + 4\ H_2O(l) \rightarrow \mathbf{FeS\ (s)} + 3\ Fe(OH)_2(s) + 2\ OH^-(aq) \rightarrow$ **Reactive iron sulfide**

Case Study – Abiotic Dechlorination at Active Mfg. Facility

- Prior bioremediation efforts / cis-1,2 DCE was primary remaining contaminant
- 2 phase treatment – No access to source under active building
- 1st phase was 26 DPT points (Z-Loy™ MicroMetal and pH modifier)
- 2nd phase was 32 DPT points (Z-Loy™ MicroMetal and pH modifier)

- No daughter product formation means abiotic system

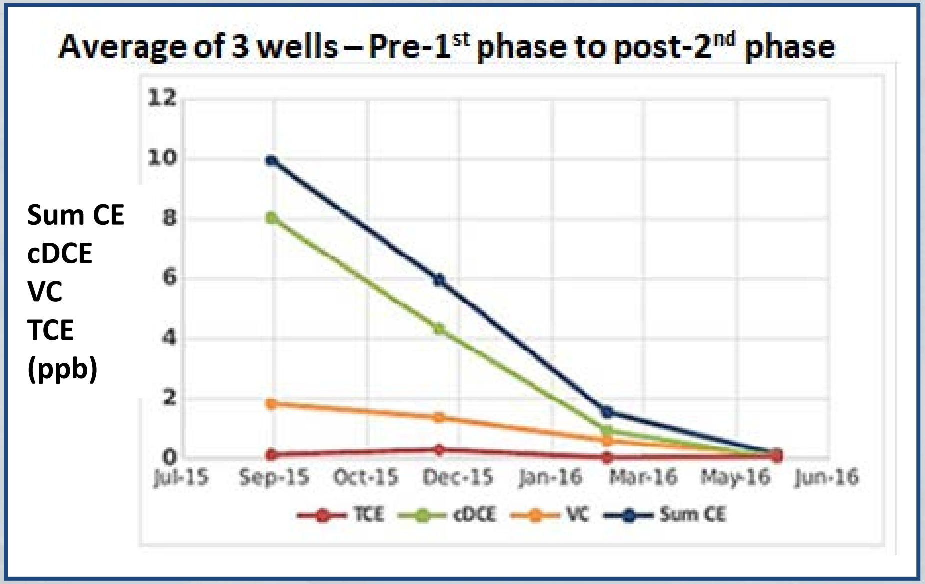
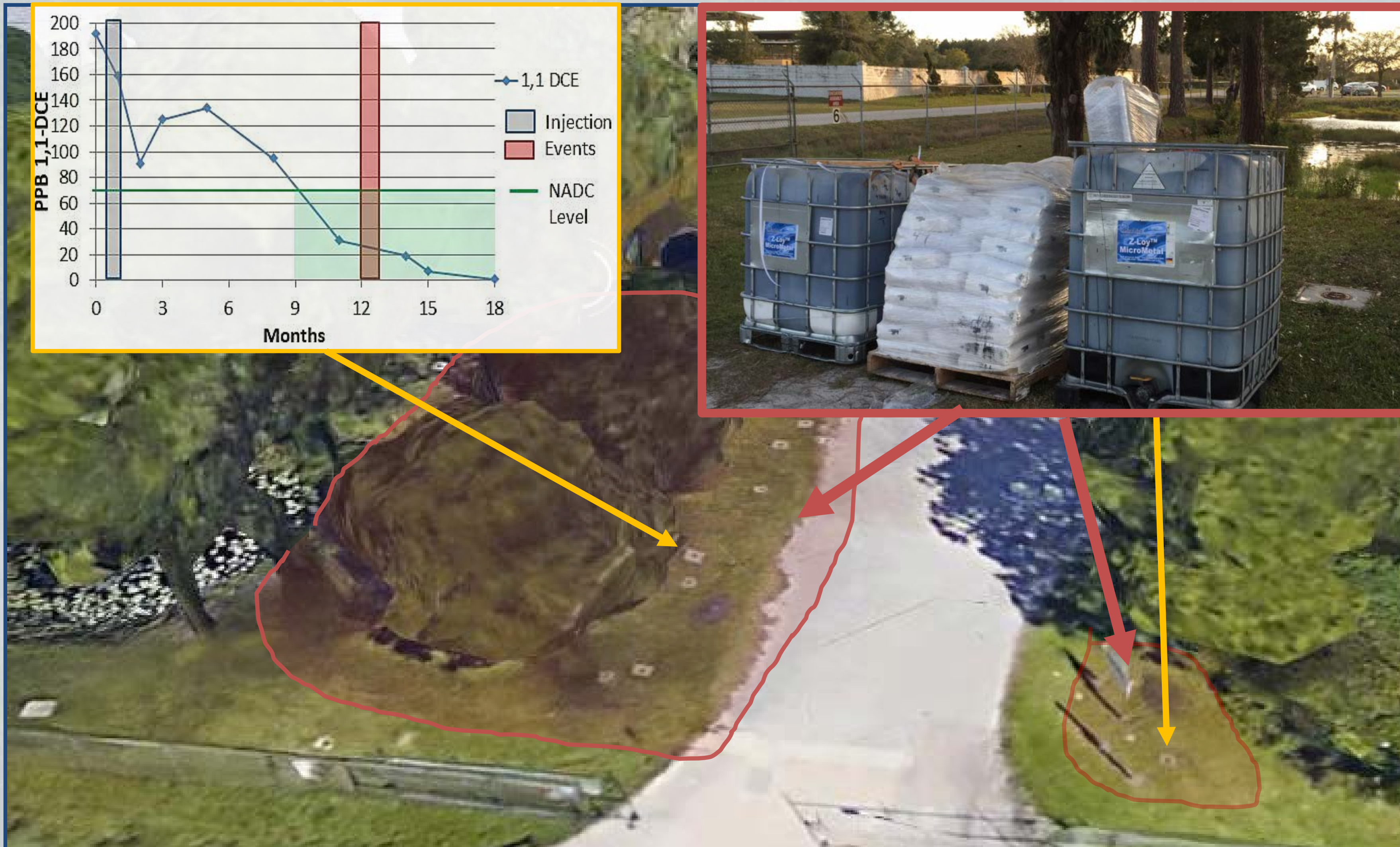
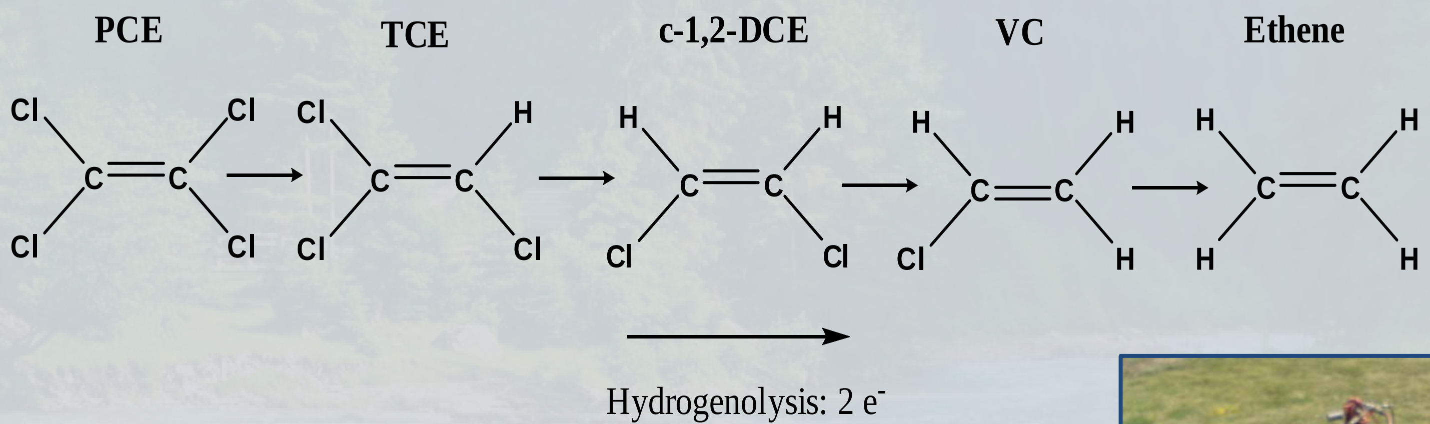


Photo: OnMaterials

Case Study – Abiotic Dechlorination at Active Mfg. Facility



Metal-Assisted Bioremediation: Biotic Degradation



Photos: OnMaterials

Co-application of:

Microbes

Case Study: Metal-Assisted Bioremediation

Source: Texas industrial site had a degreaser which ruptured spilling 100+ gal of TCE. Residual TCE DNAPL with little natural attenuation.

Photos: OnMaterials

Approach: Amendments were applied via screened wells at 5-20 psi.

Amendments:

- Z-Loy™ MicroMetal
- EVO
- pH modifier, nutrients
- Dechlorinating microbes

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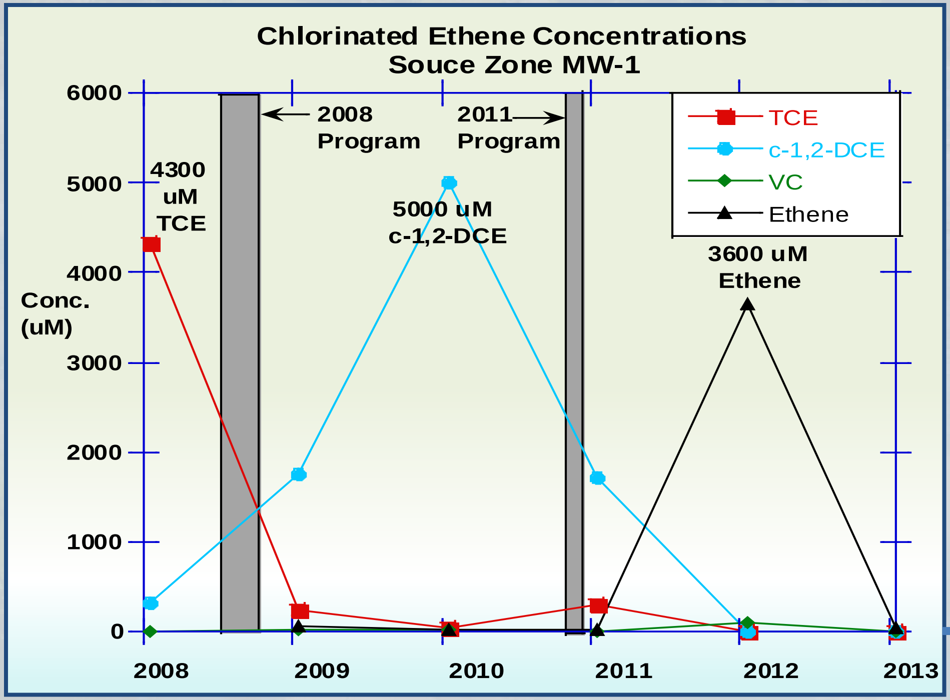
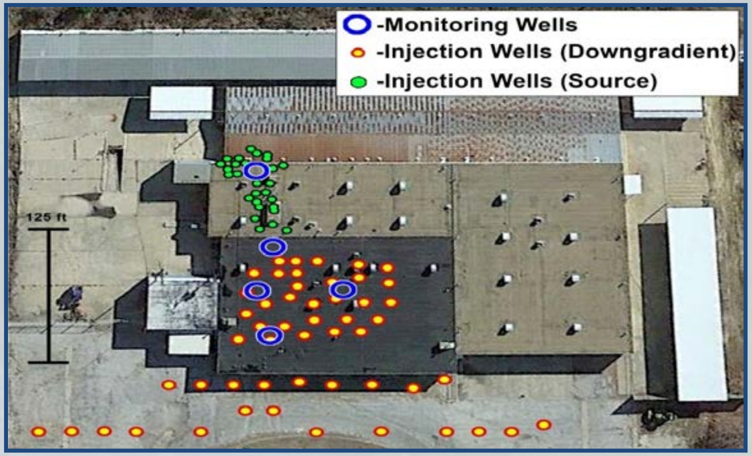
Case Study: Metal-Assisted Bioremediation

Implementation: Injection was done in two phases based on baseline and monitoring data.





Photos: OnMaterials

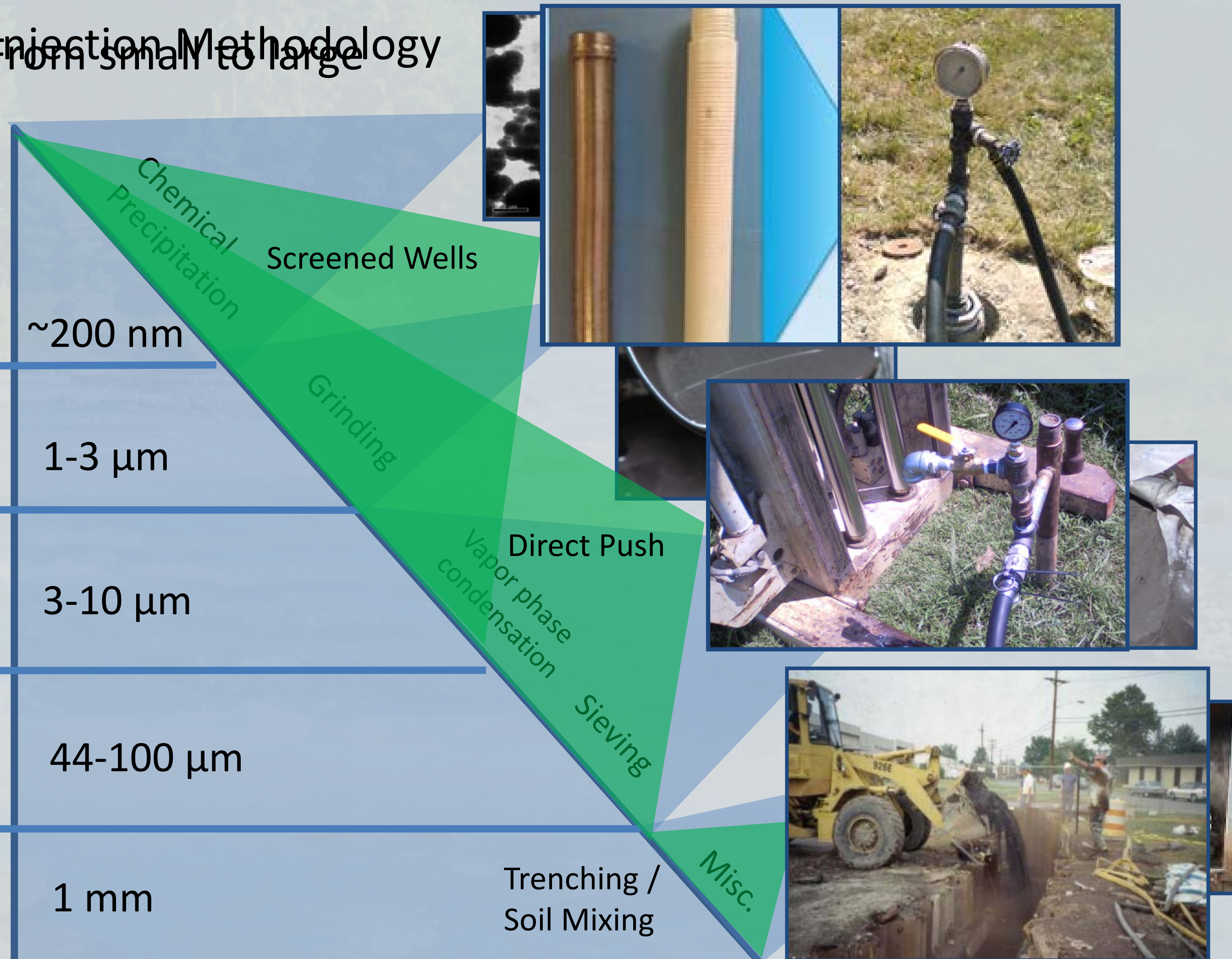
Results: 5 year monitoring data tells an interesting story. A large spike in ethene shows complete biotic degradation after 2011 injection event

Examples of Commercial Products

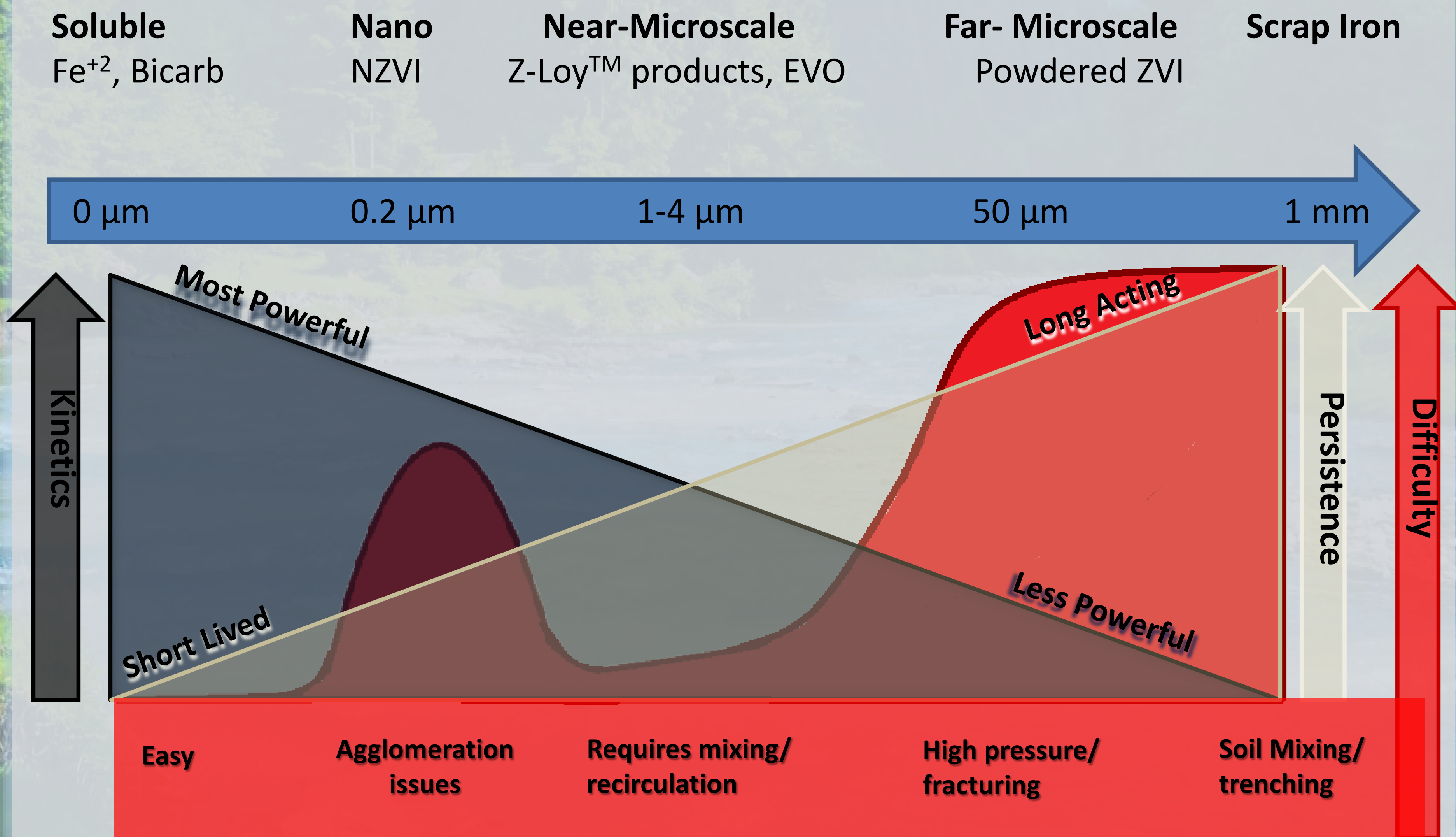
Zero Valent Iron – Injection Methodology

Zero Valent Iron – From small to large

- Soluble
- NZVI
- Z-Loy™ Products
  - OnMaterials
- Commodity Iron
  - Several vendors
- Commodity Iron
  - Several vendors
- Cast / Scrap Iron



Characteristics as a Function of Particle Size



Characteristics as a Function of Particle Size

Small particle size

- Better suspension aids in injectability and distribution
- Uniformity can be helped by adding dispersants

Large particle size

- Difficult to suspend
- Thickening with gaur, etc.
- Aggressive mixing must be done

2-3 micron Z-Loy™ AquaMetal ZVI in water

40 micron ZVI in water

Dosing Considerations

Chemical	Physical
ORP	Porosity
pH	Groundwater flow/flux
Sulfate, DO, nitrate	Saturation / Pore replacement
Contaminant & Concentration	Geology/ Lithology

- Soluble and small particle size amendments are often dosed in terms of *in-situ* concentration between **4 g/L – 25 g/L.**
- Water-like characteristics suggest that material will occupy pore space and displace / mix with groundwater when applied at low pressure.
- Large materials (40+ micron) are often dosed in terms of soil mass basis between **0.5%-2.0%.** This is usually **5x – 10x** more than small particle size.
- Higher pressures required may create fractures, therefore displacing soil/groundwater. Particle size is larger than available pore spaces.

Dosing Considerations

- Dosing for commodity and engineered iron products differs because of subsurface distribution and reactivity.

Near-nano engineered ZVI

Photo: OnMaterials

Low pressure sandbox demo

Photo: ITRC 2011

Microscale ZVI Slurry

Depiction of subsurface fractures

Optimization of Technology

- ZVI has been used since the 1990’s for remedial applications
- Materials and methods exist which take a ‘good’ technology and make it ‘great’
- Reductive dechlorination can be done with screened wells and with a small footprint using low pressure – Much easier at active facilities, neighborhoods, etc. where “low key” installation is a must.
- Enhanced reactivity means fast results

Photos: OnMaterials

Thank You for Your Time!

We offer our Z-Loy™ products as well as:

- Remedial design and support
- Injection services
- Custom mixing, material handling and injection equipment
- All personnel hold at least M.S. in Chem. or Env. Engineering discipline
- Over 15 years of successful results and expertise in the industry