Application of Reagents to Low Permeability and Fractured Media – Lessons Learned, Specific Challenges and Best Practices

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Introducing the Challenge

- Successful *In Situ* Remediation requires:
  - Sufficient dose rate based on geochemistry and COC mass
  - **Contact between reagents and COCs**
- Contact could occur directly upon product placement or occur over time via diffusion of substrates and/or contaminants
- Important to understand distribution of impacts, groundwater pathways and tailor remedial approach accordingly

Why is Low Permeable Soil and Fractured Bedrock Different??

- Low hydraulic conductivity media:
  - Silts and Clays
  - Bedrock with small fractures

Limits rate, mass and volume of reagents that can be delivered using conventional injection methods (below fracture pressure)

- Fractured media:
  - Silts and clays can have preferential pathways
  - Bedrock

Uneven contaminant distribution, difficulty in understanding and predicting connectivity

Fractured Bedrock

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- Primary and secondary porosity
- Hydraulic conductivity primarily a function of fracture numbers and sizes (secondary porosity)
- Primary porosity ranges with type of rock

Porosity in Fractured Bedrock	
Soil Type	**Total Porosity (%)**
Rocks	
Fractured basalt	5 to 50
Karst limestone	5 to 50
Sandstone	5 to 30
Limestone, dolomite	0 to 20
Shale	0 to 10
Fractured crystalline rock	0 to 10
Dense crystalline rock	0 to 5
(Freeze and Cherry, 1979)	

- How much of the bedrock is contaminated?
  - Crystalline rock—fracture surface only
  - Porous rock—varies

Key Reagent Properties

Key Reagent Properties

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The chemistry is usually well understood, the challenge is to achieve contact:

- **Injection and distribution properties:**
  - Liquid vs granular reagents dictates injection methods, transport and diffusion properties
- **Longevity:**
  - Will also impact transport and diffusion
  - The shorter lived the substrate, the more critical to achieve direct contact upon installation

Granular EHC powder – composed of microZVI and solid plant fibers

Liquid Emulsified Lecithin

Key Reagent Properties

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		Injection Properties	Distribution Properties (Solubility)	Typical Longevity	Treats
ISCO	Fentons Reagent	Liquid	Miscible	Hours to days	Wide range of COCs
	Activated Na-Persulfate	Liquid	Soluble (>500 g/L)	Weeks to Months	Wide range of COCs
	Activated K-Persulfate	Granular	Dissolves slowly (45 g/L)	Months or more	Wide range of COCs
BIO	Permeox Ultra (CaO_2)	Granular	Releases O_2 upon decomposition	9-12 months	Petroleum hydrocarbons
	Emulsified Lecithin Substrate (ELS)	Liquid	Partially transports, partially adheres	2-3 years	CVOCs
ISCR	Micro-scale ZVI (EHC)	Granular	Non soluble	5-10 years	Halogenated compounds

LONGEVITY

Estimating Reagent Dosing Requirements

Example Dosing Calculation - ISCO

- **Basic formula-Oxidant Mass for consolidated soils:**

$$[(CM_{Soil} + CM_{GW} + CM_{NAPL}) \text{ x Ratio} + SOD * \text{Soil Mass}] \text{ x S.F.}$$

Where:

- CM = Contaminant mass in the soil + groundwater + NAPL (kg)
- Ratio = Degradation or Stoichiometric ratio for contaminant (kg reagent per kg COC)
- SOD = Soil Oxidant Demand (kg Oxidant per Kg Soil)
- S.F. = Safety Factor

Example Dosing Calculation - ISCO

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- **Basic formula-Oxidant Mass for consolidated soils:**

$$[(CM_{Soil} + CM_{GW} + CM_{NAPL}) \text{ x Ratio} + \text{SOD} * \text{Soil Mass}] \text{ x S.F.}$$

Limitations with this calculation:

– Targeted treatment area often assumed as a box

– Contamination is often assumed to be evenly distributed within this box

– Reagents are assumed to evenly contact the soil

– These assumptions are rarely true for low permeability soils:

  - For overburden soil, results from HRSC may be used to refine the area beyond the "box" and subdivide it based on variations in concentrations
  - For fractured media, need to consider % soil impacted / contacted, eg. crystalline rock may primarily be impacted along the fracture surface

Modification for Fractured Media

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- **Basic formula-Oxidant Mass for Fractured Media:**

[CM x Ratio + SOD * Soil Mass * **%Contact**] x S.F.

Where:

- CM = Contaminant mass in soil + groundwater + NAPL **calculated over % soil impacted / contacted** (kg)
- Ratio = Degradation or Stoichiometric ratio for contaminant (kg reagent per kg COC)
- SOD = Soil Oxidant Demand (kg Oxidant per Kg Soil)
- **%Contact = % of soil contacted by oxidant application**
- S.F. = Safety Factor

Note: if impacts extend beyond the soil contacted, more than one application round may be needed to achieve the goals.

Application Methods and Case Studies

-Examples of applications to clay / fractured bedrock sites

Application Methods

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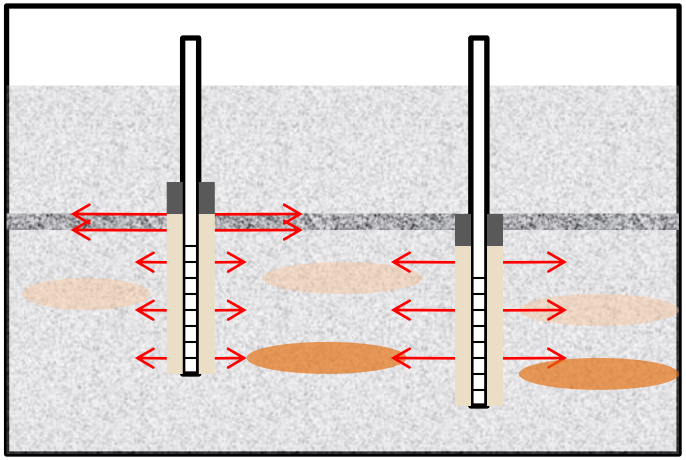
	Low Conductivity Media		Fractured Media	
	Silts and Clays	Bedrock with small fractures	Fractured Silts and Clays	Fractured Bedrock
Low pressure injections (liquid substrates only)	Limited	Limited	Yes, but limited injection volumes	Yes, but limited injection volumes
High pressure injection (fracturing)	Yes	Yes	Yes	Yes
Soil mixing	Yes	No	Yes	No

Low Pressure Injection of Liquid Substrates

Low Pressure Injection into Fractured Media

- Liquid substrates may distribute along existing fractures.
- ROI will depend on fracture connectivity



Important to isolate targeted impacted zones during application to non-heterogeneous media

Infiltration system

- Application to the source area overburden soil with the goal for vertical distribution along the same pathways as the contamination
- This approach will typically require a longer lived substrate

Case Study

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Gravity Feed of EHC Liquid for Passive Vertical Migration into Underlying Fractured Bedrock

Project location: Freeport IL

Consultant: Fehr-Graham & Associates

COC: PCE and daughters

Lithology:

- Release occurred in the overburden soil consisting of glacial till
- COI impacts now extend into the underlying weathered Galena Group dolomite to depths of *ca*. 80 ft bgs
- Groundwater at 4 ft bgs, with a downward vertical gradient

Site Map

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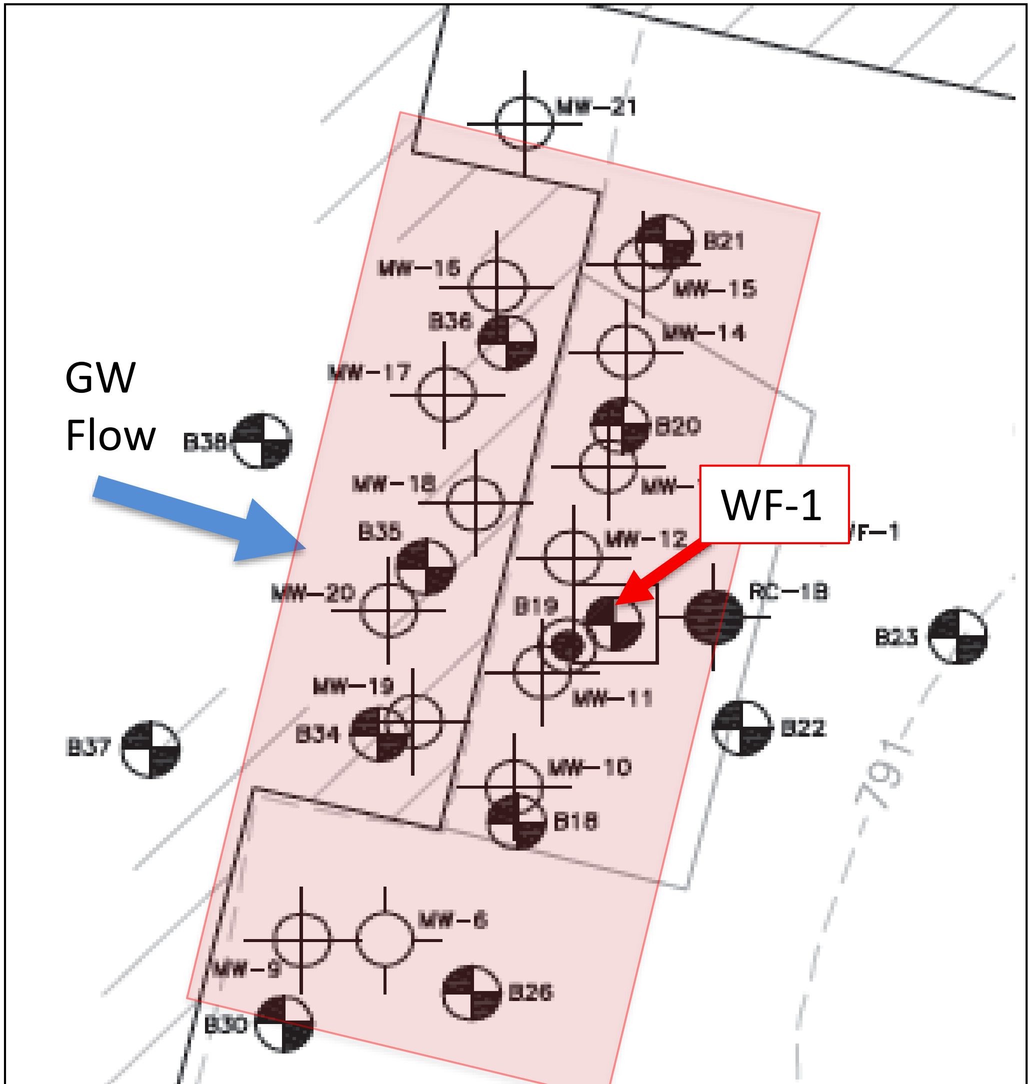

Courtesy of Fehr-Graham & Associates

Targeted Area for injection:

- ~40 ft long x 20 ft wide x 10 ft deep
- EHC-L added at 3,000 mg/L to gw

Injection wells - screened in overburden soil from 4 to 14 ft bgs

WF-1 Performance evaluation nested well screened at 4 depths down to 57.5 ft bgs

Vertical Distribution of EHC-L

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	Date Measured	ORP (mV)	Total Iron (mg/L)	TOC (mg/L)
WF-1-1 (15-17.5 ft bgs)	Baseline	-99	3.78	1.70
	Day 13	-208	93.0	605
WF-1-2 (30-31.5 ft bgs)	Baseline	-102	1.70	1.68
	Day 13	-204	89.7	655
WF-1-3 (39.5-40.5 ft bgs)	Baseline	102	0.697	<1.00
	Day 13	-121	4.13	94.8
WF-1-4 (55-57.5 ft bgs)	Baseline	49	0.537	<1.00
	Day 13	-131	1.66	147

High Pressure Injection

Injection via fracturing

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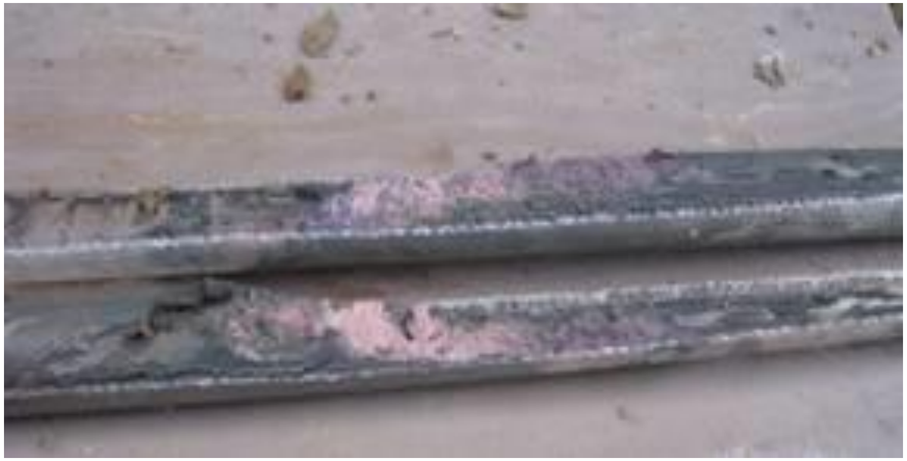
- Hydraulic and pneumatic fracturing may be performed with granular materials to expand and interconnect with existing fracture pathways:
  - ROI of ~5 ft typical for high pressure direct push.
  - ROI of up to 70 ft observed with more refined facturing methods.

Sand seam emplaced via hydraulic fracturing (courtesy of FRx)

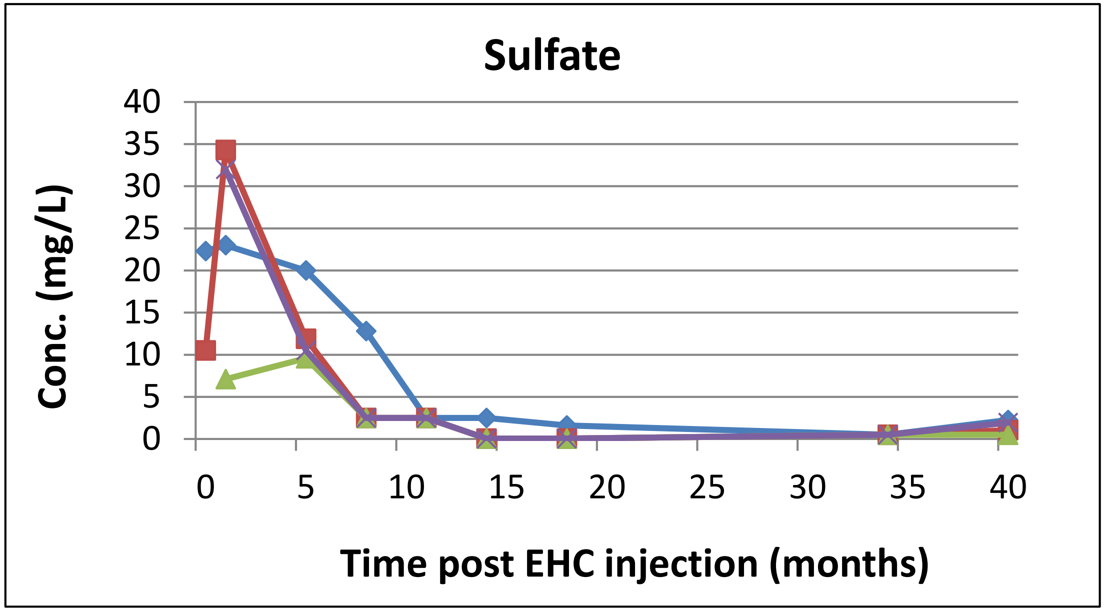
- Fracturing with for example sand could also be performed prior to application of liquid reagents
- Substrates will typically be limited in volume → low volume/ high concentration injections recommended.

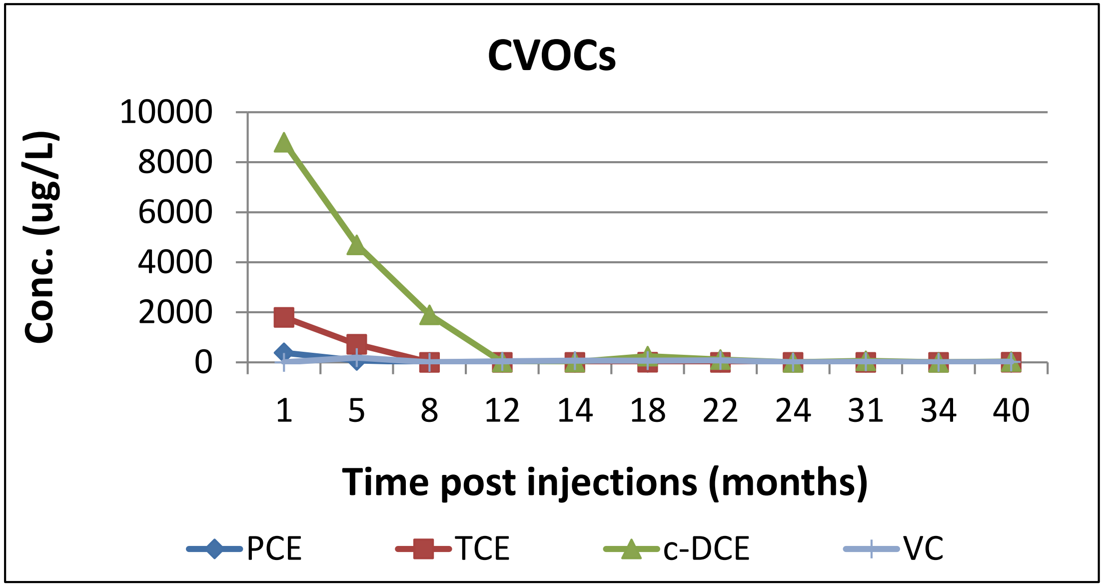
Displacement of liquid vs. solid amendments: Direct push injection test in clay soil



Solid EHC Reagent Selected based on Longevity

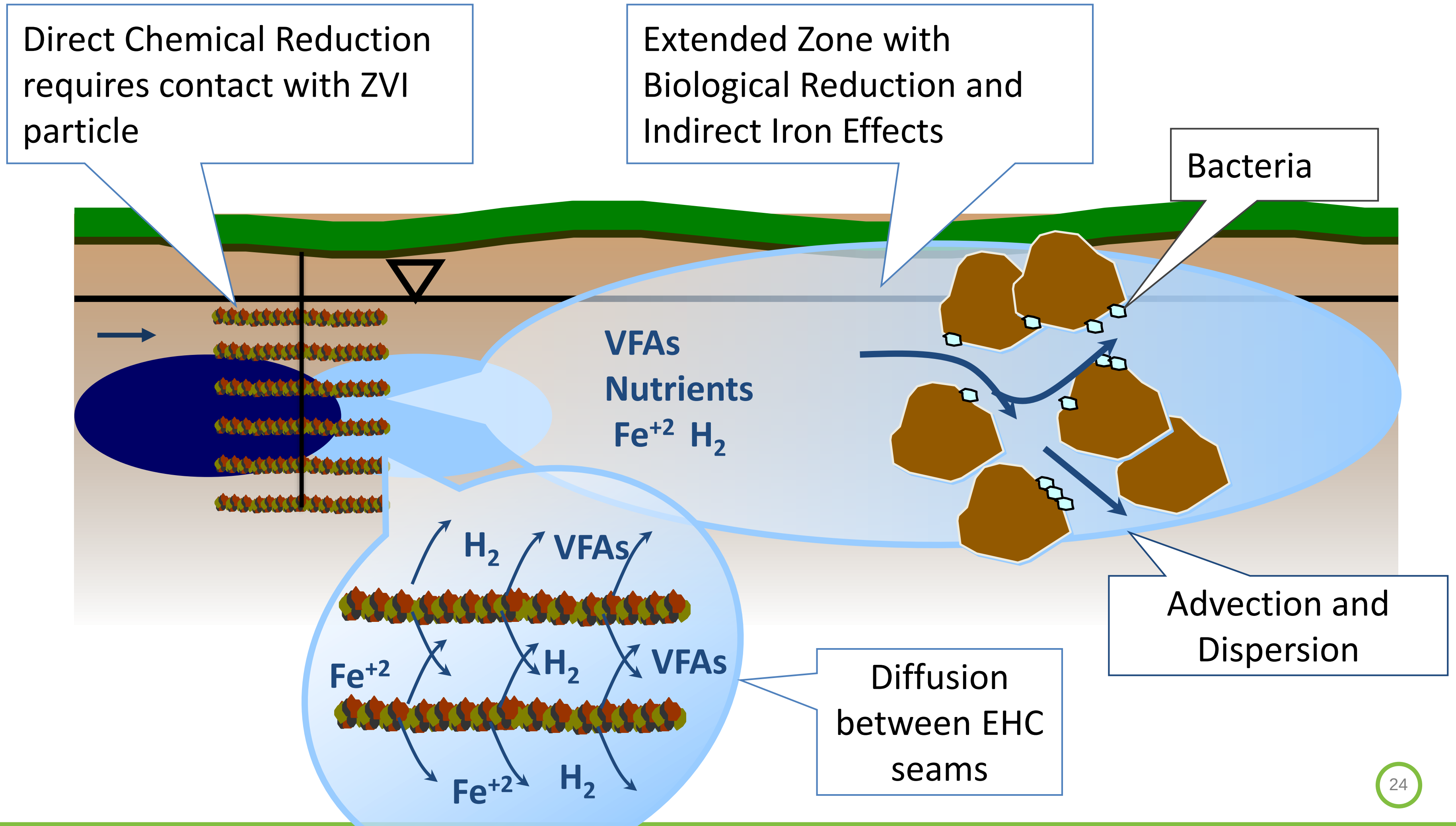
- Both substrates distributed in to discrete seams, ROI ~5 ft
- Solid ISCR Reagent selected due to its greater longevity
- Sulfate reducing conditions maintained for >40 months
- CVOCs reduced by >99%





Distribution properties of EHC

Solid reagents may still release soluble active components into groundwater over time as it decomposes



Soil Mixing

Soil Mixing for Silts and Clays

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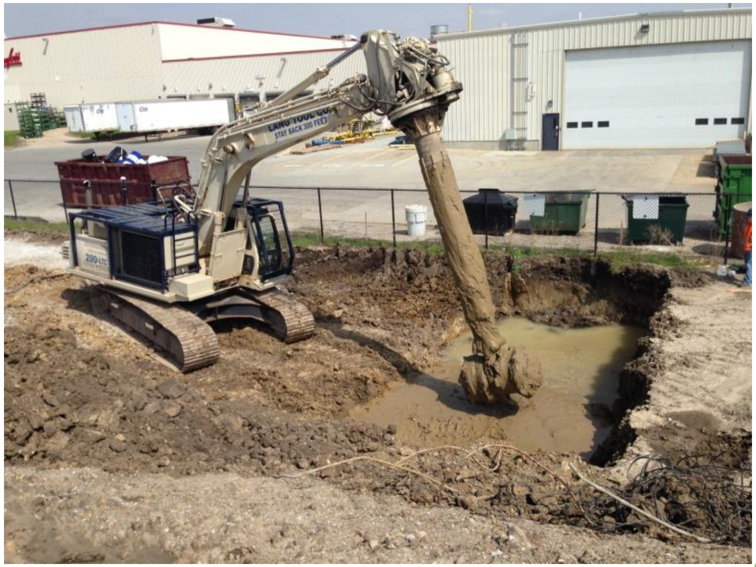
- Establish contact even with low permeable soils – highly effective with ISCO
- Hydrated lime or Portland cement may be added to stabilize soil
- Depth restrictions:
  - More standard mixing equipment down to 20 ft bgs (excavator with mixing attachment)
  - Specialized deep soil mixing equipment down to 35 ft bgs
  - Augers for deeper applications



Case Study:

Application of Alkaline Activated Persulfate via Soil Mixing

Site:

Former Manufacturing Facility WI

TCE Contamination:

Up to 140 mg/Kg

Average: 13.3 mg/Kg

Remedial goal: 1.5 mg/Kg

Lithology:

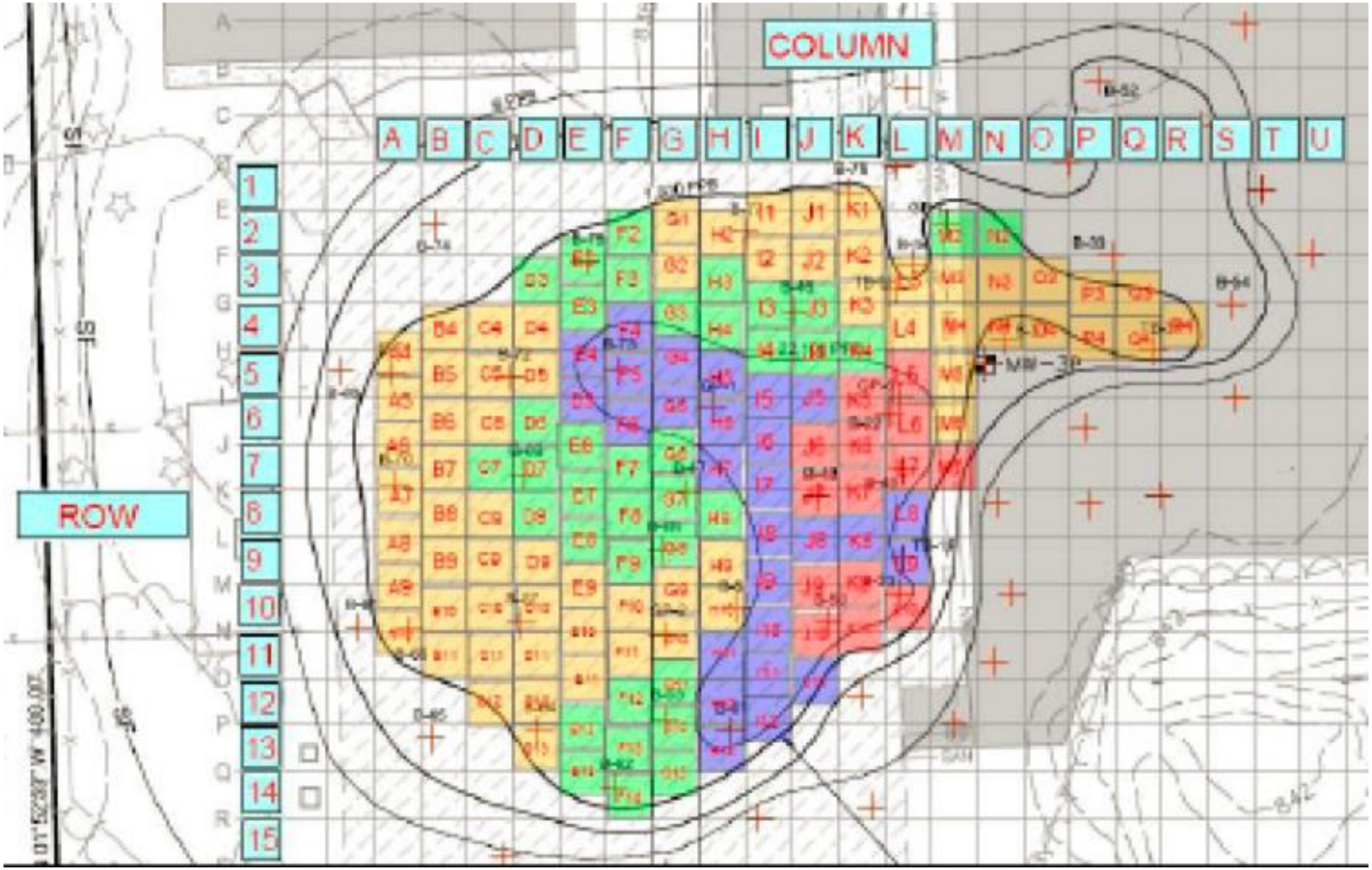
Clay; vadose zone

Courtesy of ISOTEC

Distribution of Impacts

Targeted Area Divided up into Mixing Cells

Total targeted area: 13,000 sq ft x 15 ft thick (from 0 to 15 ft bgs)



Case Study: Soil Mixing

Application:

- 170,000 lbs of Klozur persulfate distributed according with TCE conc
- 8 g Klozur persulfate per Kg soil average dose

Results:

- 36 of 37 soil samples below remedial goal
- TCE was reduced from an average of 13.3 mg/Kg to 0.084 mg/Kg (>99% reduction)

Conclusion / Summary

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- Successful remediation of low permeability sites requires:
  - Understanding of distribution of impacts and flow patterns
  - Tailor application method and reagent to achieve contact

Thank you, questions are welcome!

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