Combining Micro-Scale Zero-Valent Iron and Bioremediation to Treat Chlorinated Solvent Plumes

Presenter: Mike Lamar, PE - CDM Smith





The Problem

- In situ remediation success is the driven by:
 - Efficient amendment delivery to the contaminated zone.
 - Amendment effectiveness and longevity
- Heterogeneity / low K zones
- Fractured bedrock
- Multiple and persistent sources affect chemical mass transfer and persistence.
 - DNAPL
 - Sorption
 - Matrix back diffusion



Example Case Study – image prepared using Health Canada CSM Builder Tool 2015



Conceptual Site Model Resolution



Develop conceptual site model at an appropriate scale to account for site heterogeneity to characterize:

- Physical properties
- Contaminant of concern (COC) distribution
- Fate and transport



High-resolution site characterization tools collect data at much smaller scales (i.e., continuous to meter) with a greater data acquisition rate than conventional characterization tools and approaches.





How to plan injection into heterogeneous aquifers?

MW11RT

MW122





Optimizing Injection Strategies and In Situ Remediation Performance

Optimizing Injection Strategies and In Situ Remediation Performance (OIS-ISRP-1, 2020) Interstate Technology and Regulatory

Council (www.itrcweb.org)

SUMMI

Delivery Strategies

"Widely used = •", "Site-specific = I", and "Not applicable = NA"

Delivery Technique	Direct Push Injection (DPI) [D1]	Injection Through Wells & Boreholes [D2]	Electrokinetics This is injection through wells. [D3]	Solid Injection [<u>D4]</u>		Permeable
Hydrogeologic Characteristics <u>Unified Soil</u> <u>Classification System</u>				Hydraulic Delivery Through Wells & Boreholes [<u>D5</u>]	Pneumatic Delivery Through Open Boreholes [<u>D6</u>]	Reactive Barriers (PRBs) [D7]
Gravels	• (Sonic)	•	NA	NA	NA	•
Cobbles	• (Sonic)	•	NA	NA	NA	•
Sandy Soils (Sm, Sc, Sp, Sw)	•	•	NA			•
Silty Soils (Ml, Mh)	•		•	•	•	•
Clayey Soils (Cl, Ch, Oh)	•		•	•	•	•
Weathered Bedrock	•	•		•	•	
Competent/Fractured Bedrock	NA	•	NA			
K ≤ 10 ⁻³ to 10 ⁻⁴ (Low Perm Soils)	•		٠	٠	•	•
K ≥ 10 ⁻³ (High Perm Soils)	•	٠				٠
Depth > Direct Push Capabilities	NA	٠				

ITRC OIS-ISRP-1 Table 3-4



Determine In Situ Delivery Mechanism

Injection Wells

- Re-usable
- Simple to implement
- Limited to low viscosity / particle size amendments
- Limits ability to adapt
- Well maintenance / fouling

Direct Push Injection

- O Single event
- Some specialization
- Vertically targeted
- Limited to aqueous amendments
- Limited to certain lithology types

Fracturing

- Single event
- D Highly specialized
- Vertically targeted
- Allows wide range of amendments
- Performed with DPT or in boreholes (via packers)



Next Step: Add Amendments (Reductive Treatments)

In Situ Bioremediation

Soluble amendments (lactate, molasses)

Insoluble amendments (vegetable oils)

Solids

In Situ Chemical Reduction

Zero-valent iron

Micro-scale

Colloidal

🛈 Nano-scale

Adsorption

Activated carbonColloidal

🛈 GAC

1 PAC

Note: Amendment and delivery methods likely inter-related





Two Case Studies

- Site #1 Combined micro-scale ZVI and EVO Injection via Fracturing in Low Permeability Aquifer
- Site #2 Biorecirculation using ZVI Amended Wells in Fractured Bedrock







CASE STUDY 1 Hunters Point Naval Shipyard San Francisco, CA



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Background

- Hunters Point Naval Shipyard San Francisco, CA
- Building 258
 - Pipe manufacturing
 - Pickling and degreasing
- BRAC site cleanup to transfer property to City of San Francisco for redevelopment
- Contaminants
 - Trichloroethene (TCE) and daughters
 - Carbon tetrachloride (CT) and daughters
 - Other (e.g., trichlorofluoromethane [TCFM])
- Adaptive, multi-component treatment strategy
 - In situ chemical reduction (ISCR)
 - In situ bioremediation (ISB)





Nature and Extent of COCs

СОС	Concentration Range (µg/L)
TCE	30 – 7,800
СТ	10-140
TCFM	0.26 J – 850



Geology and Hydrogeology



- Artificial fill
- Franciscan complex bedrock
- Complex weathered and fractured waterbearing zone
 - ~12-29 feet below ground surface



Adaptive Remedial Design

- 44 locations with 5 injection intervals
- High dose
 - TCE > 110 μg/L
 - 0.004 lb/lb mZVI
 - 25 feet radius
- Low dose
 - 29 < TCE < 110, or CT >5
 - 0.0025 lb/lb mZVI
 - 30 feet radius
- Emulsified vegetable oil (EVO): 2.5% in slurry
- Bioaugmentation cultures (50% locations)



ZVI / EVO Slurry Injection

- Sonic-drilled boreholes
- Use fluid (hydraulic) pumped under pressure (150-300 psi) to a soil/rock until failure i.e., injecting) occurs
- Amendment delivery to low permeability and rock matrices
- Solid (mZVI) and liquid (EVO) amendments
- Straddle packer focuses vertical interval







& EMERGING CONTAMINANTS

Amendment Distribution: Tiltmeter Data

- Tiltmetered locations
- Plan view representation
- Averages used to model other locations



Amendment Distribution: Tiltmeter Data

- Example cross section
- 2 tiltmeter locations
- 5 vertical injection intervals



EMERGING CONTAMINANTS

Amendment Delivery: Iron, TOC



Performance Monitoring: Chlorinated Ethenes



RA Performance Assessment

- Successful amendment emplacement via slurry injections
 - Tiltmetering
 - TOC, Iron
- Successful treatment of COCs to below RGs*
 - Order of magnitude reductions in COCs
 - Anaerobic, reducing geochemistry
 - Microbial populations boosted
 - *IR28MW940F may need additional treatment; IR28MW941F still decreasing





Lessons Learned

- Adaptive approach critical to success
- Potential challenges
 - Amendment surfacing
 - Destabilized boreholes
 - ZVI clogging
 - Packer damage (bedrock)
- Open boreholes not ideal for unconsolidated material





CASE STUDY #2 Biorecirculation with ZVI-Fractured Wells Confidential Site Denver, Colorado



Site Overview

- Former industrial site
- Major infrastructure
- CVOCs (TCE) in GW follow paleochannel to northeast
- Mobile DNAPL present onsite in bedrock wells
- Historical injections
 - Traffic island infrastructure
 - Offsite biobarrier









Considerations and Constraints

- Existing infrastructure at traffic island
- Difficult hydrogeology / fractured bedrock
- Numerous access constraints (e.g,. streets, overpass)
- Significant VOC mass / DNAPL
- Large area (> 500 feet plume [TCE>1mg/L])
- High resolution characterization
 - FLUTe, geophysics, DNAPL delineation



TCE-melted NAPL test kit



Remediation Approach – Two Loops

Onsite Loop

- 3 injection locations
- 3 extraction locations
- All wells fractured with
 - Micro-scale ZVI
 - Sand
- "Pulsed" amendment injections



CONTAMINANTS

Step 1 - Environmental Fracturing

- 20 fractures (and 12 conjugate fractures) into 9 boreholes
- ~60,800 lbs of sand
- ~47,600 lbs of ZVI
- ZVI emplacement radius: 12 ft to 90 ft (40 avg)



Step 2 - Biorecirculation





Step 2 - Biorecirculation - Operational Data

ONSITE LOOP

- 6 injection wells (3 shallow/deep pairs) (with ZVI)
- 3 extraction wells (with ZVI)
- 300 feet between INJ/EXT
- 63 weeks operation
- ~500,000 recirculated GW
- ~7,000 gallons amendment injected (molasses, sodium lactate)

TRAFFIC ISLAND LOOP

- 3 injection wells (no ZVI)
- 3 extraction wells (no ZVI)
- 50-100 feet between INJ/EXT
- 59 weeks operation
- ~600,000 recirculated GW
- ~2,000 gallons amendment injected (molasses)



Performance Data – Traffic Island Loop

- Wells fractured previously (w/o ZVI)
- Historical standard EAB injections (molasses)
- Biorecirculation operation since August 2012
- Intermittent operation
 - Based on TOC concentrations
 - Hydraulic control
- Limited monitoring network
- Complete dechlorination in all wells
- System shut off





Performance Data – Onsite Loop (Shallow Bedrock)



ISUMINIT OCTOBER 3-5, 2023

Performance Data – Onsite Loop (Deep Bedrock)



Case Study #2 - Lessons Learned

- Experience in similar geology
- Environmental fracturing expertise and equipment
- Pre-design characterization
- Injection well control strategy
- Dynamic water flushing strategy
- Intermittent operation
- Adaptive management





Overall - Lessons Learned

- CSM / Pre-design characterization
- Utilize Resources to Plan
 - ITRC, AFCEC, NAVFAC, Conferences
- Utilize vendors / contractors during design
 - Two-sided discussion important
 - Get multiple perspectives
- Design for adaptability
- Do set realistic remedial goals
- Don't overestimate technology applications



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- Maleena Lemiere
- Veronica Henzi






Lucas Hellerich, PhD, PE, LEP

Optimization of a Combined Active and Passive In Situ Remediation Approach for High Concentration Metals in Groundwater

Woodard & Curran, Inc.





Co-Authors

Ramin Ansari, Lanxess, USA Nick Hastings, PG, LEP, Woodard & Curran Samantha Olney, PG, Woodard & Curran Trevor King, PE, Woodard & Curran Dan Brockmeyer, LEP, Woodard & Curran





Agenda



Conceptual site model



Technology evaluation and selection



Pilot test implementation and results

Cadmium, copper, and zinc in groundwater are discharging to surface water above criteria



CSM for metals leaching and migration



Metals solubilize in groundwater and discharge into surface water



Acidic pH increases solubility of metals



Metals concentrations exceed criteria at the river by approximately 10X - 15X



<u>SWPC</u> Cd = 12.5 ug/L Cu = 480 ug/L Zn = 6,500 ug/L



Site conditions constrain remediation options



Near river

Plume area

Source area

Extensive sub-grade rock layer is present at the base of the vadose zone source materials



HRSC, 3-D modeling and data visualization used to identify vadose and saturated zone source areas



Majority of the metals mass is in the vadose zone and at the groundwater "smear" zone











Technology evaluation and selection

Pilot test implementation and results

Multi-phase treatability study was conducted

Site media

- Groundwater
- Unsaturated (vadose) zone soil
- Saturated zone soil

Unsaturated zone

- Soil + "rainwater"
- Reduction of concentrations and leachability from soil
- Reagents (different doses)



- Conce
- Reage
 - Port
 - Ferr
 - Calc



Treatability testing for the saturated and unsaturated zones showed that calcium polysulfide (CPS), iron sulfide, and Portland Cement performed best

Saturated zone

Saturated 1 (SB-13)	Dose (% Weight)	Cd	Cu	Zn
Portland Cement	5			
Portland Cement (3%) + <u>Metafix</u> 1 (2%)	5			
Metafix 1	3			
MetaFix 1 (3%) + FerroBlack-H (1%)	4			
<u>Metafix</u> 1	7			
Metafix 1 Modified	5			
FerroBlack-H	3			
FerroBlack-H	8			
Provect-IRM (3%) + FerroBlack-H (1%)	4			
Calcium polysulfide	8			
Calcium polysulfide	12			

Unsaturated (vadose) zone

Vadose 2 (SB-15)	Dose (% Weight)	Cd	Cu	Zn	SPLP Cd	SPLP Cu	SPLP Zn
Portland Cement	5						
Portland Cement (5%) + <u>Metafix</u> 1 (2%)	7						
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> 99 % concentration reduction

< 99% and > 80% concentration reduction

< 80% concentration reduction Site-specific in situ remediation costs are significantly less than excavation and off-site disposal

Normalized Costs for Remediation Technologies





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Field pilot test – in situ solidification and stabilization (ISS) of soil and geochemical precipitation in groundwater



4% CPS 20 - 40 ft bgs

Pilot testing layout



Pilot test remediation area



Pilot test remediatio n area



Pilot test remediatio n soil mixing



Rocks ranging in size from approximately 0.5 ft to 5 ft

Soil mixing – Reductant mixing and ISS



FeS from 18 – 25 ft bgs (mostly shallower due to rock layer)



Portland Cement from 8 – 18 ft bgs





CPS provided about six months of treatment in shallow groundwater



Injection event

Calcium polysulfide results (30 – 40 ft bgs)



SB19 CPS injection area

CPS provided at least one year of



Zone of influence of treatment areas



60

Reduced concentrations of Cd, Cu, and Zn

Moderation of pH and/or reduction of ORP not observed outside of treatment areas

Approximate Zone of Influence

tixing volumes and estimated percent of the pore volume to be filled with the injected and mixing volume, in addition to the equivalent of one year of the volume of the second se

tion downgradient of the injection and mixing areas

Targeted areas of treatment appear to have resulted in about 50% concentration reductions down-gradient of the source areas

Lessons learned – full-scale design considerations

ISS formulation (8% w/w cement; 8% w/w FeS) in Area 1A achieved treatment goals

- Groundwater Cd, Cu, and Zn concentrations substantially reduced
- UCS > 50 psi
- K < 10⁻⁶ cm/s
- Extensive rock layer impeded soil mixing larger excavation cells would improve ability to mix rock
- CPS injection rates of 2 4 gpm per well (10 gpm for three wells) achieved
- Current CPS dose (4% w/w) is adequate for 30-40 ft bgs
- Higher CPS dose is required for 20-30 ft bgs

Full-scale considerations for the combined full-scale remedy

- Further focusing of soil mixing at water table interface and performing in larger cells
 - Highest flux zones
 - Where highest concentrations intersect water table
- Adaptively injecting CPS outside of source areas
 - Flexible application
 - Cost effective delivery of reductant
- Incorporation of a low permeability liner to further reduce costs
 - Can cost-effectively address pollutant mobility criteria exceedances and leachable metals in vadose zone
 - Can readily be integrated into development

Q & A

Thank you!

Lucas Hellerich

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Reducing Time of Remediation at Clay and Fractured Rock Sites: Marrying Permeability Enhancement with Remediation Chemistry

Lowell Kessel

President

CERES Remediation Products

Typical Remediation Process


Residual Mass >>> Diffusion Constraints



Diffusion Controls the **Time of Remediation-** Not the chemistry





Years for Diffusion of VOCs out of Clay



- → 3 Fracks = 1,600% reduction → 4 Fracks = 2,500% reduction

--- Undisturbed Source in Clay --- 1 Frack = 400% reduction --- 2 Fracks = 900% reduction

Reagents for Permeability Enhanced Remediation



Key Factors to Successful Use of Reagents with Proppants

Come by the poster or Booth to learn more

CERES REMEDIATION PRODUCTS



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Biochemical Destruction of Chlorinated Pesticides and Organic Explosive Compounds with Sustainable ZVI/Organic Carbon Reagents



Stacey Telesz, Fayaz Lakhwala and Alan Seech Evonik Corp.

- Daramend has been applied for more than 20 years on largescale soil remediation projects in North America, South America, Asia and Europe.
- Contaminants treated include chlorinated pesticides such as DDT, Toxaphene, and Lindane, most CVOCs, and organic explosive compounds including TNT, RDX, and HMX.
- Sustainability is an integral part of the Daramend approach to soil remediation in both the composition of the reagents and they ways they are applied during remediation.
- Daramend reagents are formulated with zero valent iron manufactured through recycling of scrap iron and food grade plant fiber that is a byproduct of grain milling.
- Our most common approaches to soil remediation with Daramend reagents are in-situ treatment of surface soil and on-site treatment of soil after excavation.
- > Both methods are considered sustainable since they eliminate transportation and off-site disposal.

Daramend[®] Bench Scale Results:

Treatment of Aldrin, Lindane, Chlordane, and Dieldrin in Louisiana soil



Chlorinated Pesticide Concentrations after Daramend® Treatment

= Aldrin = Lindane = Chlordane = Dieldrin