

SULFATE, MAGNETITE, SHEEP, AND CHLORINATED SOLVENT BIOREMEDIATION: BIODEGRADATION OF TCE IN A HIGH SULFATE FRACTURED BEDROCK ENVIRONMENT



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PRESENTATION OUTLINE

Site Description Iron and sulfate Geochemistry Background Lab Studies Pilot Test Design & Implementation Results



SITE DESCRIPTION

- Former plant site
- Electrical components manufactured from 1951-1990
- 55 acre site
- Storage and disposal of waste solvents (TCE, acetone, methanol)





SITE DESCRIPTION – GYPSUM-RICH BEDROCK LAYER



Primary GW flow in gypsum-rich D3 unit located ~46 meters deep



CHALLENGES WITH HIGH SULFATE GROUNDWATER





MICROCOSM STUDY RESULTS

- Killed controls
- Unamended
- Magnetite (Fe3O4) (Rockwood)
- Magnetite (Fe3O4) (Alfa Aesar)
- Ferric citrate
- Ferric sulfate
- Ferrous chloride
- Ferrous lactate
- Ferrous sulfate

Matis, H., et al., 2015. Laboratory Study of Iron Amendments Used to Facilitate Reductive Dechlorination of TCE in High Sulfate Groundwater, in *Proceedings of the Third International Symposium on Bioremediation and Sustainable Environmental Technologies*, Battelle Memorial Institute, Columbus, OH.





COLUMN STUDY RESULTS

Complete reductive dechlorination of TCE to ethene was achieved in bedrock columns containing EVO and magnetite under GW flow conditions

The periodic addition of supplemental nutrients and **vitamin B12** was critical to process

Availability of cobalt potentially affected by coprecipitation with iron-sulfide minerals

Harkness, M.R., et. al., 2017. Role of Iron and Vitamin B12 Amendments in Stimulating Reductive Dechlorination of TCE in High Sulfate Groundwater, in Proceedings of the Fourth International Symposium on Bioremediation and Sustainable Environmental Technologies, Battelle Memorial Institute, Columbus, OH.



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SITE DESCRIPTION

Remedy Component at Downgradient Site Boundary





INNOVATION 1: INJECTABLE FORM OF MAGNETITE







	7	P
	mL 0 ±5% 100	1000 mL <u><u>±</u>5%</u> 900
1000 mL PYREX® Made in Germany	200	800
	300	700
	400	600
	500	500
No. 1003	600	400
	700	300
	800	200
	900	100

INNOVATION 2: SLOW-RELEASE FORM OF VITAMIN B12







INNOVATION 3: SLOW-RELEASE FORM OF NITROGEN





Notes: cDCE - cis-1,2-dichloroethene mmoles/bottle - millimoles per bottle TCE - trichloroethene VC - vinyl chloride







Isodure[™] 31-0-0 isobutylidene diurea slow release fertilizer.



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GW MODELING FOR PILOT TEST DESIGN





PHASE 1 INJECTION PROGRAM SUMMARY

May 2018

Amendment	Group	Weight (lbs)	Volume (gallons)
GROUP 1			
CMAG ¹	1	1531	121
Water ²	1		120
lsodure™ (dry)³	1	8.8	N/A
MKP (dry) ³	1	2.2	N/A
Potassium bromide (dry) ³	1	2.3	N/A
GROUP 2			
EOS 100 ^{™ 4}	2	648	83.5
Water ⁴	2		1250 (350 + 900)
Microblend ^{™ 5}	2	11.0	1.2
Wilclear ^{™ 5}	2	45.9	4.1
Vitamin B12 (powder, dry) ⁶	2	0.2	N/A
DAP (dry) ⁶	2	5.5	N/A
Potassium bromide (dry) ⁶	2	3.1	N/A
Vitamin B12 (microbeads) ⁷	2	0.15	N/A

Table 1 Amendment Group Recipes (Per Batch) in Order of Addition to Tote/Tank



PHASE 1 INJECTION PROGRAM SUMMARY

Table 2: Injection Volume by Amendment Group (per individual injection event)					
Ame ndme nt	Dilution Factor	Injection Volume (gallons)			
Group 1 ¹	1:1	250			
Intermediate Chase ²	None	1000			
Group 2	15:1	1250			
Chase Water	None	10,800			

- Injections performed continuously over 72 hours
- Three amendment cycles of 24 hours each
- Total of 40,000 gallons of water (amended + chase) injected per injection well



PHASE 1 PILOT TEST SET-UP: INJECTION WATER STORAGE FRAC TANKS (21,000 GAL CAPACITY)





PHASE 1 PILOT TEST SET-UP: C-MAG GRAVITY ADDITION





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PHASE 1 PILOT TEST SET-UP: AMENDMENT MIXING TANKS





PHASE 1 PILOT TEST: VITAMIN B12 MICROBEAD ADDITION





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PERFORMANCE MONITORING

Short-term amendment distribution

Intermediate-term monitoring

- Collect real-time data using down-hole probes (waterlevel, pH, DO, ORP, conductivity, temperature, turbidity)
- Support real-time data using periodic laboratory analyses (potassium, bromide, iron, TOC, cobalt)

 VOCs, CSIA, field parameters (pH, DO, ORP), MNA parameters (nitrate, dissolved iron, sulfate, sulfide, dissolved gases)

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D3 PILOT TEST – PHASE 1 LAYOUT



PROBE WATER LEVEL DATA

CMAG/EVO Injections

Phase 1 Pilot -Week 1





PROBE PH DATA

CMAG/EVO Injections Phase 1 Pilot -Week 1





PROBE ORP DATA

CMAG/EVO Injections Phase 1 Pilot -Week 1





PROBE TURBIDITY DATA

CMAG/EVO Injections

Phase 1 Pilot -Week 1





PROBE TEMPERATURE DATA

CMAG/EVO Injections

Phase 1 Pilot -Week 1







CMAG/EVO Injections Phase 1 Pilot -Week 1

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LABORATORY COBALT DATA

CMAG/EVO Injections Phase 1 Pilot -

Week 1





D3 PILOT TEST – PHASE 1 LAYOUT



PROBE TURBIDITY DATA

CMAG/EVO Injections Phase 1 Pilot -Week 2





LABORATORY IRON DATA

Injections Phase 1 Pilot -Week 2

CMAG/EVO





LABORATORY COBALT DATA

CMAG/EVO Injections Pilot Week 2





LONGER-TERM PERFORMANCE MONITORING VOCS IN WELL B-31D3



LONGER-TERM PERFORMANCE MONITORING CSIA IN WELL B-31D3

Date	δ ¹³ C TCE	δ^{13} C cDCE	δ ¹³ C VC
7/9/2013	-22.8	-28.2	-30
11/2/2015	-22.4	-27.8	
7/26/2016	-22.5	-28.1	
8/2/2017	-20.6	-26.4	-31.9
8/2/2018	-9.5	-21.7	-24.5



CONCLUSIONS AND NEXT STEPS

Conclusions

Next Steps

- Injection program successful at injecting amendments
- Injection well spacing of 40feet verified in pilot test
- Observed accelerated reductive dichlorination of TCE

- Eight additional injection wells installed in fall 2018 (treatment zone now 400 feet wide)
- Phase 2 injections will occur in spring/summer 2019



THANK YOU

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