APPLICATION OF TIME-RELEASE ELECTRON DONORS AND ELECTRON ACCEPTORS FOR ACCELERATED BIOREMEDIATION

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ABSTRACT

There are limited options for cost-effective approaches to remediate soil and groundwater contamination. One technology that has proven its potential involves the use of time-release electron acceptors to accelerate bioattenuation of aerobically degradable compounds and time-release electron donors to accelerate the natural bioattenuation of anaerobically degradable compounds. This technology enjoys its reputation as a sensible strategy for engineering accelerated bioattenuation because it consistently delivers results while 1) minimizing design, capital, and management costs and 2) allowing for the engineering of a low-impact application, invisible-remediation process.

Oxygen Release Compound (ORC®) is a proprietary formulation of intercalated magnesium peroxide that slowly releases oxygen for up to a year. This facilitates the aerobic degradation of environmental contaminants including petroleum hydrocarbons, certain chlorinated hydrocarbons, ether oxygenates, and triazine herbicides.

Hydrogen Release Compound (HRC®) is a proprietary, food-grade polylactate ester. Upon being deposited into an aquifer, HRC slowly releases lactic acid for one to two years that ferments to hydrogen. Hydrogen donates electrons that drive reductive bioattenuation processes. Compounds degraded by reductive dehalogenation include perchloroethene, trichloroethane, carbon tetrachloride, and their daughter products; pentachlorophenol; and herbicides and pesticides such as dieldrin, dichloropropane, alachlor, and metolachlor. HRC has been used on over 300 sites, which we believe makes it the most widely used electron donor for accelerating bioattenuation.

Key words: HRC, ORC, reductive dechlorination, oxygen, herbicides, pesticides, pentachlorophenol
Application of Time-Release Electron Donors and Electron Acceptors for Accelerated Bioremediation

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**ORC®**

Oxygen Release Compound

A proprietary time release formulation of magnesium peroxide

\( \text{MgO}_2 \)

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**Oxygen Release Compound Chemistry**

- \( \text{MgO}_2 + \text{H}_2\text{O} \rightarrow \frac{1}{2} \text{O}_2 \uparrow + \text{Mg(OH)}_2 \)
- Extended oxygen release profile (6-12 months)
- \( \text{Mg(OH)}_2 \) – a safe end product
- Mg compounds are insoluble
Intercalated vs. Unintercalated Peroxygens

- Unintercalated peroxyn is subject to "oxygen lock-up!"

Unintercalated

- "Rad Formation"
- O₂ Trapped
- Mg(OH)₂

Intercalated

- Rad is Disrupted
- O₂ Released
- Mg(OH)₂
- PO₄

ORC has been applied on over 7,500 sites in 50 states & 12 countries

HRC®
Hydrogen Release Compound
A proprietary time release formulation of polylactate ester

Hydrogen Release Compound, HRC™
- HRC is a polylactate ester
- When hydrated, HRC time-releases lactic acid
- HRC accelerates anaerobic bioremediation of CHCs such as PCE, TCE, and TCA
  - Microbes metabolize lactic acid to other organic acid intermediates, such as acetic acid
  - Hydrogen is released as a by-product
- This hydrogen facilitates reductive dechlorination of chlorinated hydrocarbons
Formation of an Ester

Alcohol + Lactic Acid → Lactate Ester

H₂O + CH₃-CH(OH)-CH₂-OH → CH₃-C(=O)-OH

Polylactate Ester

HRC-Glycerol Polylactate (GPL)

Using HRC to Promote Biological Reductive Dechlorination of CAHs

- HRC, once deposited into the subsurface, slowly releases lactic acid.
- Anaerobic bacteria metabolize the lactic acid as a nutrient source.
- Hydrogen is released as a byproduct and can be used for reductive dechlorination of CAHs.
HRC Field Application

HRC is a viscous but injectable substance. HRC is injected into the aquifer using direct-push technologies.

The Benefits of a Persistent, Time-Release Hydrogen Source

- Allows for passive chlorinated hydrocarbons (CHs) remediation (1+ year activity)
- Cost-Effective
  - Reduces capital costs in comparison with other technologies
  - Remains in place for continuous hydrogen delivery and continued savings on O&M costs
- Non-invasive, leaves no above-ground disturbance

Applications by Contaminant

- Chlorinated Hydrocarbon Solvents
- Nitroaromatics
- Oxygenics
- Other Anaerobically Degradable Compounds
  - Insecticides
  - Herbicides
  - Fumigants
HRC has been applied on 350 sites in 50 states

75% of all sites treated biologically

Agriculture Related Contaminants
Treatable via ORC and HRC

Chlorinated insecticides:
chloroame, aldrin, chlordane, heptachlor, lindane (HRC)

Herbicides:
azine and other triazine herbicides (ORC), dirocyb (HRC)

Chloroacetamide herbicides:
aloxy, meoalooxy, acetochlor (ORC/HRC)

Fumigants:
di- and tri-chloromonomers, carbon tetachloride (HRC)

Wood preservatives:
penachlorophenol (ORC/HRC), copper chromium/arsenic (HRC)

Biodegradation of Chlorinated Insecticides

Ref: Rittmann and McCarty, Environmental Biotechnology (2001)
Biodegradation of Agriculture Related Chlorinated Contaminants

"Commonly recognized now is that reductive dehalogenation occurs with strongly reducing anaerobic conditions for essentially all chlorinated aromatic and aliphatic compounds."

"Indeed, all of the pesticides,... except heptachlor epoxide, were [rapidly] transformed under anaerobic methanogenic conditions."

From: Rittmann and McCarty, Environmental Biotechnology (2001)

Chlordane Biodegradation: Field Application

SITE:
- chlordane plume in an aquifer in North Carolina
- an HRC barrier was installed perpendicular to groundwater flow across the 20 feet wide plume (treatment thickness was 5 to 25 feet bgs)

RESULTS:
- in-barner monitoring well: chlordane decreased from 2090 ppb to 232 ppb (89%) in 23 months
- upgradient monitoring well: minimal chlordane decrease from 617 ppb to 576 ppb

Biodegradation of Carbon Tetrachloride

- Carbon tetrachloride reductive dechlorination is similar to that for other chlorinated hydrocarbons.
- Laboratory treatability studies for carbon tetrachloride with HRC were successful.
Biodegradation of Carbon Tetrachloride

Carbon Tetrachloride

CCl₄

Chloroform
CHCl₃

Dichloromethane
CH₂Cl₂

Chloromethane
CH₂Cl

Carbon dioxide, water, chloride
CO₂+H₂O+Cl⁻

Adapted from Gidwani, Y.P. et al. (1998) Natural attenuation of tetrachloroethene and chlorinated solvents in the Superfund, in Proc. 1998

Carbon Tetrachloride Biodegradation: Field Application

SIT:  
- carbon tetrachloride and other chlorinated solvent plume in an aquifer in Indiana  
- HRC applied to site

RESULTS:  
- carbon tetrachloride decreased from 190 ppb to 81 ppb (57%) in 8.5 months in the HRC-impacted well  
- other chlorinated solvent concentration decreased as well

Other Field and Laboratory Work

- At a site in Oregon, dinoseb decreased 67% in 6.5 months after HRC application.
- At a site in California, CI- and tri-chloropropane each decreased 80% in 15 months after HRC application.
- An HRC/ORC side-by-side pilot treatability field test is being performed for bioremediation of a mixed plume of metolachlor, alachlor, acetochlor, and dimethenamid.
Other Field and Laboratory Work

- Laboratory treatability studies for dieldrin with HRC were successful.
- At a site in Alabama, HRC will be used to treat soil contaminated with chlordane, aldrin, dieldrin, heptachlor, and toxaphene.

ORC Case Histories

ORC Barrier Slurry
Vancouver, Washington

- Operating retail service station contaminated with BTEX and GRD.
- Estimated hydrocarbon mass was 33 lbs.
- Groundwater flow West at 3 ft/day
- ORC barrier treatment was composed of 15 bore holes placed 10 feet on center and located along the downgradient property boundary.
- About 65 lbs. of ORC were applied into each borehole via a hollow stem auger drill rig.
ORC Barrier Slurry
Vancouver, Washington
Conclusion

- There was an overall mass reduction of 43% for BTEX, 71% for benzene, and 52% for ORC in five months.
- Actionable BTEX level in the sentinel well at the leading edge of the plume (MWI-11) was reduced 95%.
- The client’s total cost was $40,000. This represented a savings of $210,000 versus alternative designs.

ORC Injection Array Treatment
San Francisco, California

- Downtown real estate construction site had groundwater contamination of BTEX
- Groundwater flow South up to 0.15 m/day
- Aquifer consists of silt and sandy silt
- Approximately 2,500 lbs. of ORC slurry were injected into 50 push points for treatment using a cone penetrometer rig due to extremely tight "bay muds."
Reduction of BTEX in MW-4
San Francisco, California

ORC Injection Array Treatment
San Francisco, California
Conclusion

After five months:
- BTEX decreased 55% in MW-1 (source area)
- BTEX decreased 100% in the wells immediately downgradient of ORC injection
- Regulators recognized ORC significantly reduced the contaminant source mass and granted a "no further action required"
- The client's cost of product and application cost was approx. $25,000. This represented a savings of $150,000 versus alternative designs.

Quantifying Enhanced Natural Attenuation

\( \frac{dC}{dt} = -kC \)  
Reduction of concentration with time

Upon integration

\( C = C_0 e^{-kt} \)  
where \( C = \) final Concentration
\( C_0 = \) initial Concentration
\( k = \) rate constant
\( t = \) time

\( k = \ln \left( \frac{C_0}{C} \right) / t \)

- ORC was installed at a convenience store site in MI undergoing a renovation.
- Contamination levels before and after ORC application in sentinel well MW 2 were recorded.
- 3,000 lbs. of ORC were applied via 54 points.

Rates

ORC Source Treatment (STEX)
Dexter, Michigan

Historic change before ORC was 3800 ppm to 2500 ppm at 1340 days

\[
\ln \left( \frac{3800}{2500} \right) = \frac{1340}{x} = 0.0007
\]

water ORC injection the contaminant went from 2500 ppm to 500 ppm in another 346 days

\[
\ln \left( \frac{2500}{500} \right) = \frac{346}{x} = 0.0048
\]

Rate difference:

\[
\frac{0.0048}{0.0007} = 16 x
\]

Reduction in Contaminant Concentration
with 16x rate difference
Conclusions

- ORC has been shown over the last several years to be a highly effective management tool at sites contaminated with several classes of aerobically degradable compounds.

- The technology works optimally when used on properly characterized sites and where the primary objective is to accelerate natural attenuation. Quantifying this statement we usually see at least an order of magnitude of rate improvement. MCL’s can be achieved as a function of starting concentrations, rates and the time available to meet those goals.

Conclusions

- Other collateral benefits accompany the use of simple push-pull point deposition of the material and these include the virtual elimination of design and capital costs. O&M essentially consists of making one or more re-applications if necessary.

- Additional benefits include ease of application and management and the fact that the treatment operates silently below ground, which has particular importance at active sites.
HRC Case Histories

HRC Field Demonstration in WI: Site Map

HRC Field Demonstration in WI
HRC injection diagram overlaying hydrogen concentration map at day 149

HRC Application results in increased hydrogen concentrations in the aquifer, 2-8 nM

LEGEND
- HRC injection points (spaced 3” on center)
- Monitoring well locations

SCALE (feet)
0 5 10
Whittaker Ordnance Facility - Hollister, CA

Site Characteristics and Application
- HRC pilot test at an Ordnance Facility
- Aquifer consists of medium to fine silty sand
- Application thickness = 15 ft, GW velocity = 20 ft/yr
- Contaminated with TCE, TCA, Perchlorate at levels of approximately 4,500 ug/L, Chrome 6 and Fr-113 at levels of approximately 220-300 ug/L
- 660 lb of HRC injected into aquifer via direct push, points spaced 5' on center
HRC vs. Other Organic Substrates

- In theory all organic substrates are fermentable to hydrogen. However, there are some important differences with respect to:
  - solubility
  - longevity
  - the potential to produce $H_2$ at a proper rate
  - the total amount of $H_2$ that can be produced per mole