Slow Release Persulfate and MultiOx™ Cylinders for Passive, Long-term Treatment of Petroleum Hydrocarbon Contaminated Sites

Jean Paré
Chemco Inc.

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Slow Release Persulphate and MultiOx™
Cylinders for Passive, Long-term Treatment of
Petroleum Hydrocarbon and Organic
Contaminants Contaminated Sites

Pamela Dugan, Ph.D., P.G.; Carus Corporation
Jean Paré, P. Eng.; Chemco Inc.

Presentation Agenda

• Permeable Reactive Barrier - Definition & Usage
• Sustained-Release (SR) Technology Overview:
  ➢ Permanganate Cylinder
  ➢ Unactivated Persulphate Cylinder
  ➢ Combinations of Reactants MultiOx™
• Experimental and Laboratory Validation:
  ➢ Batch Kinetic Tests
  ➢ 1-D Columns Experiments
• Engineering Design Tool Overview
• Questions
Permeable Reactive Barrier (PRB) Definition & Usage

- PRB are used as an in situ permeable treatment zone designed to intercept and remediate a contaminant plume. PRBs have become an important component among the various technologies available to remediate groundwater contamination.

- PRB is an evolving technology with new and innovative reactive materials introduced to treat different contaminants as well as innovative construction methods. “New” reactive materials include mulch for treating chlorinated solvents, metals, and energetic and munitions compounds, zeolites for treating radionuclides and heavy metals.

- Sustained Release Technology (SR) allow the use of oxidants for organic contaminants and petroleum hydrocarbons control and removal.

Source: ITRC - Permeable Reactive Barrier: Technology Update – June 2011
Sustained-Release (SR) Technology Concept

- Can easily be coupled with many existing treatment technologies
- Minimizes above-ground infrastructure at active sites
- Long-term presence of oxidants can mitigate the impacts of matrix diffusion (release can last up to 12 months)
- Cost-effective, and can be implement as part of a stepped-implementation strategy
- Use natural groundwater gradients to deliver oxidants

Minimizes Site Disruption

- Traditional ChemOx Permanganate Footprint
Minimizes Site Disruption

- Reduced Cylinder Site Impact

Oxidant Release Mechanism

- As the oxidant solids dissolve void spaces are created
Oxidant Release Mechanism

- Newly created void spaces expose additional oxidant solids for dissolution and diffusion
- Process occurs radially from the exterior of the cylinder to the inner core

Oxidant Release Mechanism

- Initial spike of permanganate in time
- Slower and lower release of permanganate at later times
Oxidant Release Characteristics - Permanganate

Permanganate Release from 3 Diameters RemOx SR Cylinders
0.27, 1.35 and 2.5 inch
Length 1-inch, Flow rate 0.7 mL/min

Measured permanganate concentrations match model!

Permanganate Blend MultioX™
(PERSULFATE + PERMANGANATE)
CYLINDER TECHNOLOGY
DEVELOPMENT
Physical Properties

Sodium Persulphate
- Molar Mass: 238.10
- Density: 2.40 g/cm$^3$
- Solubility: 556 g/L

Potassium Permanganate
- Molar Mass: 158.03
- Density: 2.703 g/cm$^3$
- Solubility: 63.8 g/L

Oxidant Release Characteristics - Persulphate

Release data was fit to simple Gaussian Distribution Model

\[ f(t) = A \frac{1}{\sigma \sqrt{2\pi}} e^{-\frac{(t-t_0)^2}{2\sigma^2}} \]
Permanganate + Persulphate respective profile

Permanganate

Persulphate

Oxidant Release Characteristics

MultiOx SR

Oxidant Release Conclusions

- Permanganate release is characterized by high initial concentration, followed by long-term and sustained release
  - Release rates can be modeled using an analytical solution
  - Release rates can be scaled and quantified
- Persulphate exhibits a different oxidant release profile than permanganate
  - Particle Size differences?
  - Crystalline packing differences?
  - Solubility
- The combination of persulphate and permanganate in MultiOx results in both:
  - Improved oxidant release characteristics and
  - Provides multiple oxidants for contaminant degradation

Laboratory Study - Unactivated Persulfate
BTEX Batch Kinetic Tests

*Batch kinetic experiments were performed to:*
1. Determine the natural oxidant demand kinetics of unactivated persulphate
2. Determine the kinetic rate of contaminant degradation by unactivated persulphate
3. Use these results to design a 1-D column experiment

*The experimental approach for batch kinetic experiments:*
- Performed in sacrificial 40-mL VOA vials
- At each time point, duplicate vials were sacrificed and oxidant/COCs were measured
- BTEX/MTBE (~ 10 ppm) and unactivated persulfate or Multiox (100, 1000, and 10,000 ppm)
1-D Column Experimental Design

Experimental approach:
- 1-D Columns (2 inch ID x 48 inch length or 4 inch ID x 48 inch length)
- Control columns - DI water influent, packed with ASTM-graded silica sand or North Island Site soil (San Diego)
- Treated columns - BTEX influent prepared in deionized water (~6 ppm), packed with ASTM-graded silica sand or North Island Site soil
- Persulfate SR Permanganate SR or MultiOx SR cylinders - Three 1.35 inch diameter pieces, 1 inch long pieces or One 3-inch diameter piece
- Flow rate (0.04 mL/min), seepage velocity (0.32 ft/day), ~5-8 day retention time (depending on column ID)

1-D Column Results–BTEX Removal–Persulphate SR

Removal Efficiencies: Benzene: 85.3%–98.3%, Toluene: 84.6%–96.6%, Ethylbenzene: 94.6%–99.3%, Xylene: 94.6%–99.3% over the 40-day experiment
**Experimental Conclusions**

- **Persulphate**
  - Exhibited sufficient reactivity with benzene, toluene, ethylbenzene, and xylene, dioxane and VOCs

- **MultiOx**
  - Increased reactivity with benzene, toluene, ethylbenzene, xylene, Dioxane and VOCs (not presented)

- 1-D columns validated the application of SR cylinders for remediation of BTEX, dioxane & VOCs

- Natural activation mechanisms (thermal, Fe, Mn, other transition metals) may enhance persulphate reaction kinetics
SR Cylinder Development

3 Type of SR Cylinder Available

- **Potassium Permanganate** - RemOx® SR ISCO Reagent: KMnO₄ based product dispersed in a solid matrix, (~80% w/w)
- **Sodium Persulfate SR**: NaS₂O₈ based product dispersed in a solid matrix (~73% w/w)

Cylinder Dimension Available

- 18 inches long (1.35 or 2.5 inch diameter) –
- Containing either 0.87 to 10.5 kg of oxidant per unit

Site Positioning via

- Borehole with sand
- 3 feet long holder (2 cylinders)
- Deployed via DPT or in wells
SR Deployment Strategies

- Possible Configurations:
  - Permeable reactive barrier (PRB)
    (1 to 3 feet radius offset recommended)
  - Permeable reactive zone/grid (PRZ)
  - Trench
  - Funnel and gate

SR Engineering Design Tool

Design Factors

- Site characteristics (2nd Order NOD, groundwater velocity, porosity, type of contaminants and concentrations)
- Oxidant Type and Diameter
- Oxidant release rate(s)
- Contaminant Reaction Kinetics
- Treatment Objectives
- Tool will have costing information for cylinder site deployment either using DPT or wells

Note: Available for Permanganate SR, Persulfate SR and MultiOx SR to be released (possibly by end of the year)
SR Engineering Design Tool

Cost estimates for DPT or well emplacement
Conclusions

- MultiOx, Permanganate and Persulphate SR represent a novel delivery strategy for plume treatment
  - Effective at removing a variety of COCs (e.g., 1,4 Dioxane, BTEX, VOCs, phenols, PAHs, PHC F2-F4)
  - Sustained oxidant persistence can address "rebound" and back-diffusion
  - Active industrial/commercial facilities: passive in situ treatment without above ground equipment/infrastructure
- Unactivated persulphate kinetics may vary, so we recommend performing contaminant kinetic and NOD treatability tests
- Additional Contaminants Treatability Testing Data underway
About our Expertise, Products and Services

- **Training and Education**: technical transfer session, health and safety training;
- **Consulting and Technology Site Assessment**: technology support and selection (chemical oxidation and reduction, co solvent-surfactant soil washing and enhanced bioremediation);
- **Products supply, logistic and storage**: nutrients, bacterial preparations strains, oxidants, reducing agents, catalysts, oxygen and hydrogen release compounds, co solvent-surfactant blends
- **Laboratory Services and Analysis**: Groundwater Parameter Analysis, Tracer Study, Soil and Groundwater Oxidant Demand Evaluation (SOD), Bench Scale Treatability testing in saturated and unsaturated conditions.

Thank you for your attention!

Questions?

Contact information:
E-mail: jean.pare@chemco-inc.com // Pamela.Dugan@caruscorporation.com
Tel: 418-953-3480 // (815) 224-6870