In Situ Chemical Oxidation (ISCO): Prospects for the Use of Potassium Permanganate in São Paulo State

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Overview of Remediation Technologies

Most recent developments have involved the application of a treatment agent.

- Geochemical Fixation
- Zero Val Iron
- Reductive Dechlorination
- In Situ Chem. Oxidation
- Air Sparging
- Soil Vapor Extraction
- In Situ Aerobic Bioremediation
- Excavation / Pump & Treat
## In Situ Chemical Oxidation: Permanganate

**Formula** - $\text{KMnO}_4$ $\text{NaMnO}_4$

**Molecular Weight** - 158.04g K; 141.9 Na

**Equivalent Weight** - 52.6g K; 47.3 Na

**Color** - Purple; Visible pink color in water at ~0.5ppm

**Solubility** - K - 64g/l @ 20°C; 250g/l @ 65°C

Na - >400 g/L @ 20°C

**Application** - Wells, Geoprobe

1-10% Solutions

**Contaminants** - PAHs, Phenols (PCP), TEX, chloroethenes, MTBE
Permanganate Color

Most noticeable feature - distinctive purple color

Limit of visible detection ~ 0.25 ppm (lab)
Color saturation occurs ~ 100 ppm cannot discern > conc. visually
Permanganate Concentration, milligrams KMnO₄ / Liter = ppm

Note: ppm x 10,000 = %
Typical geology in São Paulo metropolitan area (weathered Gneiss)
Contaminant transport in heterogeneous porous media

1. Convection through mobile pore space / major fractures
2. Diffusion into immobile pore space / rock matrix
Contaminant Removal

Diffusion gradient of contaminant decreases over time, resulting in “tailing” and possible “rebound”

1. Initial situation
2. Start of remediation
3. End of remediation
In Situ Contaminant Destruction

Diffusion gradient of treatment agent remains high, resulting in destruction of contaminant in both mobile and immobile pore space.

1. Initial situation  
2. Start of remediation  
3. End of remediation
Oxidation of chloroethenes with $\text{KMnO}_4$

Tetrachloroethene

$$4\text{KMnO}_4 + 3\text{C}_2\text{Cl}_4 \rightarrow 6\text{CO}_2 + 4\text{MnO}_2 + 4\text{KCl} + 8\text{HCl}$$

Trichloroethene

$$2\text{KMnO}_4 + \text{C}_2\text{Cl}_3\text{H} \rightarrow 2\text{CO}_2 + 2\text{MnO}_2 + 2\text{KCl} + \text{HCl}$$

Dichloroethene

$$8\text{KMnO}_4 + 3\text{C}_2\text{H}_2\text{Cl}_2 \rightarrow 6\text{CO}_2 + 8\text{MnO}_2 + 8\text{K}^+ + 6\text{Cl}^- + 2\text{OH}^- + 2\text{H}_2\text{O}$$

Vinyl chloride

$$10\text{KMnO}_4 + 3\text{C}_2\text{H}_3\text{Cl} \rightarrow 6\text{CO}_2 + 10\text{MnO}_2 + 10\text{K}^+ + 3\text{Cl}^- + 7\text{OH}^- + \text{H}_2\text{O}$$
Chemical Oxidation vs. Biological Reduction for Remediation of Chloroethenes

Some of the advantages of permanganate:

• No hazardous byproducts are formed (such as methane gas or vinyl chloride);
• Proven reactivity;
• KMnO₄ is stable (>1 year);
• Easy to import, not protected by patents;
• Generally faster than biological processes; and
• Destroys DNAPL ganglia.
Permanganate reacts with everything in the soil.

Soil Oxidant Demand (SOD) = demand from non-target analytes and reactions with soil matrix:

- Natural Organic Matter
- Sulfides
- Reduced Metals

SOD (gram $\text{KMnO}_4$ / kilogram of soil) needs to be measured in laboratory tests in order to assess the feasibility of using permanganate.
Development of SOD test facility in Brazil

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SOD test results in São Paulo State

- **Alluvial Tertiary Sediments - São José dos Campos**
  - 6 to 9 m depth: 0.04 to 0.08 gr KMnO₄ / kg soil
  - 9 to 12 m depth: 0.15 to 0.34 gr KMnO₄ / kg soil

- **Weathered Gneiss - Cotia**
  - 25 to 35 m depth: 0.13 to 0.54 gr KMnO₄ / kg soil

- **Alluvial Tertiary Sediments - Limeira**
  - 10 to 20 m depth: 0.29 to 0.86 gr KMnO₄ / kg soil

Average SOD = 0.3 gr KMnO₄ / kg soil
Average cost of KMnO₄ purchase = R$ 5 / m³ soil
Oxidant Injection Methods

1. Circulation/Migration
   - Advection
   - Dispersion

2. Emplacement
   - Displacement
   - Advection
   - Dispersion

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Field Application – Injection Well

Typical injection rates of 200L / hour are feasible in most tested soils, due to existence of preferential flow paths - as measured by constant head injection tests.
Field Application – Direct Push (Geoprobe)

Limited by depth and soil type

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Field application – Soil sample inspection after injection

Soil sample B-6, 7 to 8 meters below ground surface
Conclusions

• All tested soils exhibit a low Soil Oxidant Demand (SOD) for KMnO₄;
• All tested soils exhibit sufficiently high injection rates for the application of water-based oxidants;
• Potentially many sites in São Paulo State contaminated with chloroethenes can be remediated with KMnO₄ in a cost-effective way;
• Applicable to contamination in sediments, weathered rock and fractured rock.