In Situ Chemical Oxidation ad Bioremnediation

The application of in-situ chemical oxidation (ISCO) technologies, which are based on the delivery of oxidizing agents to contaminated source zones in order to oxidize contaminants into harmless end products within the soil mass, is a promising method for remediation of multiple contaminants. Typical oxidants used traditionally have included potassium permanganate, hydrogen peroxide (Fenton’s reagent) and ozone. Each of these oxidants has its limitations (e.g. persistence, reactivity etc.) within a soil matrix. Klozur® perosulfate (\( \text{Na}_2\text{S}_2\text{O}_8 \)) is a more recent addition to the list of possible oxidants for use within ISCO applications and possesses multiple advantages as compared to more traditional oxidants.

1. Direct Oxidation:

\[
\text{S}_2\text{O}_8^{2-} + 2\text{H}^+ \rightarrow 2\text{HSO}_4^{-}
\]

A stoichiometric equation can be derived e.g. for PCE

\[
25\text{PCE} + 2\text{C}_4\text{H}_4\text{O}_6 + 4\text{H}_2\text{O} \rightarrow 2\text{C}_2\text{O}_4^{2-} + 4\text{CO}_2 + 4\text{H}^+ + 4\text{H}_2\text{O}
\]

\( \text{kg}^{-1}/\text{g} \)

2. Radical Formation

\[
\text{S}_2\text{O}_8^{2-} \rightarrow \text{SO}_4^{2-} + \text{OH}^{-}
\]

“Klozur CR (Combined Remedy)”

**Properties**

- Formulated as a slurry
- pH ~ 11

**Typical Applications**

- Direct push injection
- Emplacement (excavations, barrier walls)

**Target Compounds**

TPH, BTEX, MTBE, PAHs
- Chlorobenzenes, Phenols etc.

**Conclusions**

- Activated perosulfate will not sterilize soil / groundwater
- 20 – 30% initial drop in microbial population observed for both aerobic and anaerobic species
- Reduction of microbial species observed, sometimes greater than initial concentrations
- Cell utilization of contaminant substrate will be influenced but not halted
- Calcium peroxide – activated perosulfate is effective on TPH / BTEX compounds
- SBR’s can be stimulated by residual sulfur

**Impact of ISCO on Sulfate Reducing Bacteria (SRBs)**

- Contaminated sediments from Kalamazoo River
- Initial contaminant loadings: 7720 mg/kg PCB
  - 1063 mg/kg PAHs
  - 175 µg/kg total Hg
- Study incorporated 3 dosages
  - 4 g Klozur®/kg sediment
  - 10 g Klozur®/kg sediment
  - 20 g Klozur®/kg sediment

A study of the ability of Klozur perosulfate to degrade recalcitrant organic compounds including PCBs and PAHs in addition to methyl mercury (Methyl), was performed using contaminated sediments in a stirred tank reactor (pictured above). The higher the dose of perosulfate caused significant contaminant destruction. However, following treatment the microbial population in the reactor was re-established and sulfate reducing bacteria were seen to recognise the reaction vessel. The sulphate produced from biological activity also complexed the mercury, removing it from solution.

**Examples of Contaminants Destroyed by Klozur Perosulfate**

- Chlorinated Solvents
  - PCE, TCE, DCE
  - TCA, DCA
  - Vinyl Chloride
- Carbon tetrachloride
- Chloroform
- Chlorothene
- Chloromethane
- Dichloromethane
- Trichloropropane
- Methylene chloride
- Freons
- Oxygenates
  - MTBE
  - TBA
- Phenols
  - phenol
  - Pentachlorophenol
  - 2,4-Dichlorophenol
- TPHs
  - Anthracene
  - BTEX
  - Benzo(a)pyrene
  - Benzo(c)pyrene
- Benzene
  - Napthalene
  - Pyrene
- Naphthalene
- Toluene
- Ethylbenzenes
- Chlorobenzenes
  - Chlorobenzene
  - Dichlorobenzene
- Methylene chloride
- Toluene
- DDT
- Chloride
- Hexachlorobenzene
- Lindane
- Toxaphene
- Dieldrin
- Permethrin

**Conclusions**

- No Methyl produced in Klozur® CR oxidized all contaminants in a sediment high in NOM (>14%) Native SBR survived the highest dose (20 g/kg) and thrived soon afterwards
- SBR produced sulfide within weeks
- >80% of Hg precipitated as HgS after 30 weeks

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