Fe-EDTA (Dissolvine E-F3-13)

1. Stacey Telesz, FMC Corporation
2. Ferric sodium EDTA; Ethylenediaminetetraacetic acid, ferric sodium complex
3. MSDS Sheet Attached
4. Number of field applications – 200+
5. Case Studies – Attached
6. Technical Summary - Ethylenediaminetetraacetic acid, widely abbreviated as EDTA is an aminopolycarboxylic acid and a colorless, water-soluble solid. Its conjugate base is named ethylenediaminetetraacetate. Its usefulness arises because of its role as a hexadentate (“six-toothed”) ligand and chelating agent, i.e. its ability to "sequester" metal ions such as Ca^{2+} and Fe^{3+}. After being bound by EDTA, metal ions remain in solution but exhibit diminished reactivity. EDTA is produced as several salts, notably disodium EDTA and calcium disodium EDTA. Also, used as an activator for Persulfate and hydrogen peroxide.
Material Safety Data Sheet
Dissolvine® E-FE-13

1. PRODUCT AND COMPANY IDENTIFICATION

Product name: Dissolvine® E-FE-13
Synonyms: Ferric sodium EDTA; CHEMICAL NAME: Ethyldiaminetetraacetic acid, ferric sodium complex
Formula: C10H12FeN2O8Na.3H2O

Recommended use: Chelating agent; Plant nutrient

Manufacturer: Akzo Nobel Functional Chemicals LLC
525 West Van Buren Street
Chicago, IL 60607-3823
Phone 1 800 / 906-7979

Emergency telephone number: For leak, fire, spill or accident emergencies, call:
1 800 / 424 9300 (CHEMTREC - U.S.A.)
1 703 / 527 3887 (CHEMTREC - Collect - All Other Countries)
1 613/ 996-6666 (CANUTEC - Canada)

Medical / Handling Emergencies:
1 914 / 693-6946 (Akzo Nobel - U.S.A.)

2. Hazards identification

Emergency Overview:

Yellow-green odorless powder
Fine dust dispersed in air in sufficient concentrations, and in the presence of an ignition source, is a potential dust explosion hazard.

Potential health effects:

- Eyes: Product dust may cause mechanical eye irritation.
- Skin: Substance may cause slight skin irritation.
- Inhalation: Inhalation of dust in high concentration may cause irritation of respiratory system.
- Ingestion: No known effect based on information supplied.

Chronic Toxicity: In a 31/61-day oral study on rats with Ferric-sodium EDTA, the NOAEL >/= 84 mg/kg.

3. Composition/information on ingredients

<table>
<thead>
<tr>
<th>Chemical Name</th>
<th>CAS-No</th>
<th>Weight %</th>
</tr>
</thead>
<tbody>
<tr>
<td>EDTA ferric sodium complex</td>
<td>15708-41-5</td>
<td>87-89</td>
</tr>
<tr>
<td>Water</td>
<td>7732-18-5</td>
<td>11-13</td>
</tr>
</tbody>
</table>
### 4. First aid measures

**Eye contact**
In case of eye contact, remove contact lenses and rinse immediately with plenty of water, also under the eyelids, for at least 15 minutes. Get medical attention if irritation persists.

**Skin contact**
Wash off with warm water and soap. Wash contaminated clothing before reuse. Get medical attention if irritation develops and persists.

**Inhalation**
Move to fresh air. If breathing difficulty or discomfort occurs and persists, obtain medical attention.

**Ingestion**
Rinse mouth with water and afterwards drink plenty of water or milk. Do not induce vomiting or give anything by mouth to an unconscious person. Get medical attention if symptoms occur.

### 5. Fire-fighting measures

**Flammable properties**
Not combustible.

**Suitable extinguishing media**
Use CO2, dry chemical, or foam. Soft stream or water fog only if necessary.

**Explosion Data**
- Sensitivity to Mechanical Impact: Not sensitive.
- Sensitivity to Static Discharge: Not sensitive.

**Specific hazards arising from the chemical**
Avoid generating dust; fine dust dispersed in air in sufficient concentrations, and in the presence of an ignition source is a potential dust explosion hazard.

**Protective equipment and precautions for firefighters**
As in any fire, wear self-contained breathing apparatus and full protective gear.

<table>
<thead>
<tr>
<th>NFPA</th>
<th>Health Hazard</th>
<th>Flammability</th>
<th>Stability</th>
<th>Special Hazards</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1</td>
<td>1</td>
<td>0</td>
<td>-</td>
</tr>
</tbody>
</table>

### 6. Accidental release measures

**Personal precautions**
Avoid contact with the skin and the eyes. Powder becomes slippery when wet. For personal protection see section 8.

**Methods for containment**
Cover with plastic sheet to prevent spreading. Do not allow material to enter storm or sanitary sewer system. Use a wet sweeping compound or water to prevent dust formation. Sweep or vacuum up spillage and return to container. Material may be recycled when contamination is not a problem.

**Methods for cleaning up**
After cleaning, flush away traces with water. Dispose of waste as indicated in Section 13.

### 7. Handling and storage

**Handling**
Avoid dust formation. Use in well ventilated areas to prevent formation of explosive dust-air mixtures. Avoid inhalation and prolonged and/or repeated skin and eye contact.

**Storage**
Keep tightly closed in a dry and cool place. Containers should not be opened until ready to use. Store in original container. Keep at temperatures below 25°C. Keep away from incompatible materials (see Section 10).
8. Exposure controls/personal protection

Exposure guidelines

<table>
<thead>
<tr>
<th>Chemical Name</th>
<th>ACGIH TLV</th>
<th>OSHA PEL</th>
<th>NIOSH</th>
<th>Mexico</th>
</tr>
</thead>
<tbody>
<tr>
<td>EDTA ferric sodium complex 15708-41-5</td>
<td>TWA: 1 mg/m³</td>
<td>TWA: 1 mg/m³</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Chemical Name</th>
<th>British Columbia</th>
<th>Quebec</th>
<th>Ontario TWAEV</th>
<th>Alberta</th>
</tr>
</thead>
<tbody>
<tr>
<td>EDTA ferric sodium complex 15708-41-5</td>
<td>TWA: 1 mg/m³</td>
<td>TWA: 1.0 mg/m³</td>
<td></td>
<td>TWA: 1 mg/m³</td>
</tr>
</tbody>
</table>

Occupational exposure controls

Engineering measures
Apply technical measures to comply with the occupational exposure limits. When working in confined spaces (tanks, containers, etc.), ensure that there is a supply of air suitable for breathing and wear the recommended equipment.

General Information
If the product is used in mixtures, it is recommended that you contact the appropriate protective equipment suppliers. These recommendations apply to the product as supplied.

Respiratory protection
Whenever dust in the worker's breathing zone cannot be controlled with ventilation or other engineering means, workers should wear respirators or dust masks approved by NIOSH/MSHA, EU CEN or comparable organization to protect against airborne dust.

Eye/face protection
Tightly fitting safety goggles

Skin and body protection
Wear suitable protective clothing. Protective shoes or boots.

Hand protection
Protective gloves: Nitrile rubber.

Hygiene measures
When using, do not eat, drink or smoke. Wash hands and face before breaks and immediately after handling the product.

9. Physical and chemical properties

9.1 Information on basic physical and chemical properties

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Appearance</td>
<td>Yellow to green powder</td>
</tr>
<tr>
<td>Physical state</td>
<td>solid</td>
</tr>
<tr>
<td>Odor</td>
<td>odorless</td>
</tr>
<tr>
<td>pH</td>
<td>(1% solution) 4 - 5.5</td>
</tr>
<tr>
<td>Melting Point/Range</td>
<td>80 °C (crystal water loss)</td>
</tr>
<tr>
<td>Freezing point</td>
<td>No information available.</td>
</tr>
<tr>
<td>Boiling Point/Range</td>
<td>not applicable</td>
</tr>
<tr>
<td>Flash Point</td>
<td>not applicable</td>
</tr>
<tr>
<td>Evaporation rate</td>
<td>not applicable</td>
</tr>
<tr>
<td>Flammable properties</td>
<td>Not combustible</td>
</tr>
<tr>
<td>Vapor pressure</td>
<td>No information available.</td>
</tr>
<tr>
<td>Vapor density</td>
<td>No information available.</td>
</tr>
<tr>
<td>Density</td>
<td>0.95 g/cm³</td>
</tr>
<tr>
<td>Water solubility</td>
<td>90 g/L @ 20 °C; 300 g/L @ 80 °C</td>
</tr>
<tr>
<td>Percent volatile</td>
<td>No information available.</td>
</tr>
<tr>
<td>Partition coefficient:</td>
<td>log Pow = &lt;1</td>
</tr>
<tr>
<td>Viscosity</td>
<td>No information available.</td>
</tr>
</tbody>
</table>

9.2 Other information

Autoignition Temperature
> 200 °C
10. Stability and reactivity

<table>
<thead>
<tr>
<th>Stability</th>
<th>Stable under recommended storage conditions.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Conditions to avoid</td>
<td>Temperatures above 25°C. Very hygroscopic; protect from moisture.</td>
</tr>
<tr>
<td>Hazardous decomposition products</td>
<td>Thermal decomposition can lead to release of irritating and toxic gases and vapors: nitrogen oxides (NOx), Carbon oxides, metal oxides.</td>
</tr>
<tr>
<td>Hazardous polymerization</td>
<td>Hazardous polymerization does not occur.</td>
</tr>
</tbody>
</table>

11. Toxicological information

<table>
<thead>
<tr>
<th>Acute effects</th>
<th>Non-irritating.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Eye irritation</td>
<td>Non-irritating to the skin</td>
</tr>
<tr>
<td>Skin irritation</td>
<td></td>
</tr>
<tr>
<td>LD50 Oral</td>
<td>&gt; 2000 mg/kg bw (rat)</td>
</tr>
<tr>
<td>LD50 Dermal</td>
<td>&gt; 2000 mg/kg bw (rat)</td>
</tr>
<tr>
<td>LC50 Inhalation:</td>
<td>&gt; 2.75 mg/L (4-hr)</td>
</tr>
<tr>
<td>Sensitization</td>
<td>Did not cause sensitization on laboratory animals.</td>
</tr>
</tbody>
</table>

**Chronic Toxicity**

- In a 31/61-day oral study on rats with Ferric-sodium EDTA, the NOAEL \( \geq 84 \) mg/kg.

**Carcinogenicity**

- Not recognized as carcinogenic by Research Agencies (IARC, NTP, OSHA, ACGIH)

**Mutagenicity**

- Not mutagenic in Ames Test. Ferric sodium EDTA gave a positive response in the Mouse Lymphoma Assay (in vitro) with and without metabolic activation at concentrations that were cytotoxic. The positive response was attributed to a possible sensitivity of the cells to abnormal iron concentrations.

**Reproductive toxicity**

- EDTA and its sodium salts have been reported, in some studies, to cause birth defects in laboratory animals only at exaggerated doses that were toxic to the mother. These effects are likely associated with zinc deficiency due to chelation. Exposures having no effect on the mother should have no effect on the fetus. Based on data with a related substance (magnesium-disodium EDTA), the NOAEL is expected to be 500 mg/kg.

**Target Organ Effects**

- Skin, Eyes.
12. Ecological information

Ecotoxicity

Active Ingredient(s)
EDTA ferric sodium complex (15708-41-5)

<table>
<thead>
<tr>
<th>Active Ingredient(s)</th>
<th>Duration</th>
<th>Species</th>
<th>Value</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ferric Sodium EDTA</td>
<td>96 h LC50</td>
<td>Rainbow trout</td>
<td>&gt;100</td>
<td>mg/L</td>
</tr>
<tr>
<td>Ferric Sodium EDTA</td>
<td>35 day NOEC.</td>
<td>Zebra fish</td>
<td>28.9</td>
<td>mg/L</td>
</tr>
<tr>
<td>Ferric Sodium EDTA</td>
<td>48 h EC50</td>
<td>Daphnia magna</td>
<td>100.9</td>
<td>mg/L</td>
</tr>
<tr>
<td>Ferric Sodium EDTA</td>
<td>21 day NOEC.</td>
<td>Daphnia magna</td>
<td>31</td>
<td>mg/L</td>
</tr>
<tr>
<td>Ferric Sodium EDTA</td>
<td>72 h NOEC.</td>
<td>Algae</td>
<td>69.9</td>
<td>mg/L</td>
</tr>
</tbody>
</table>

Persistence and degradability
Inherently biodegradable. EDTA ferric-sodium complex is photodegradable with a half life of 20 days.

Bioaccumulation
Bioaccumulation is unlikely.

Mobility
Will likely be mobile in the environment due to its water solubility. C.O.D. is approximately 570 mg/g.

<table>
<thead>
<tr>
<th>Chemical Name</th>
<th>log Pow</th>
</tr>
</thead>
<tbody>
<tr>
<td>EDTA ferric sodium complex</td>
<td>-10.6</td>
</tr>
</tbody>
</table>

13. Disposal considerations

Waste disposal methods
This material, as supplied, is not a hazardous waste according to Federal regulations (40 CFR 261). This material could become a hazardous waste if it is mixed with or otherwise comes in contact with a hazardous waste, if chemical additions are made to this material, or if the material is processed or otherwise altered. Consult 40 CFR 261 to determine whether the altered material is a hazardous waste. Consult the appropriate state, regional, or local regulations for additional requirements.

Contaminated packaging
Cleaning the container before final disposal is the responsibility of the person disposing of the container. Empty containers should be taken to an approved waste handling site for recycling or disposal.

14. Transport information

<table>
<thead>
<tr>
<th>DOT</th>
<th>not regulated</th>
</tr>
</thead>
<tbody>
<tr>
<td>TDG</td>
<td>not regulated</td>
</tr>
<tr>
<td>ICAO/IATA</td>
<td>not regulated</td>
</tr>
<tr>
<td>IMDG/IMO</td>
<td>not regulated</td>
</tr>
</tbody>
</table>
15. Regulatory information

International Inventories
TSCA Inventory (United States of America)  Complies
DSL (Canada)  Complies
NDSL (Canada)  Complies
EINECS/ELINCS (Europe)  Complies
ENCS (Japan)  Complies
IECSC (China)  Complies
KECL (Korea)  Complies
PICCS (Philippines)  Complies
AICS (Australia)  Complies
NZIoC (New Zealand)  Complies

U.S. Federal Regulations
SARA 313
Section 313 of Title III of the Superfund Amendments and Reauthorization Act of 1986 (SARA). This product does not contain any chemicals which are subject to the reporting requirements of the Act and Title 40 of the Code of Federal Regulations, Part 372.

SARA 311/312 Hazard Categories
Acute Health Hazard  no
Chronic Health Hazard  no
Fire Hazard  no
Sudden Release of Pressure Hazard  no
Reactive Hazard  no

CERCLA
This material, as supplied, does not contain any substances regulated as hazardous substances under the Comprehensive Environmental Response Compensation and Liability Act (CERCLA) (40 CFR 302) or the Superfund Amendments and Reauthorization Act (SARA) (40 CFR 355). There may be specific reporting requirements at the local, regional, or state level pertaining to releases of this material.

International Regulations
Mexico - Grade  Slight risk, Grade 1
Canada
This product has been classified in accordance with the hazard criteria of the Controlled Products Regulations (CPR) and the MSDS contains all the information required by the CPR.
WHMIS Hazard Class
Non-controlled

16. Other information

<table>
<thead>
<tr>
<th>HMIS</th>
<th>Health Hazard 1</th>
<th>Flammability 1</th>
<th>Stability 0</th>
<th>Special precautions -</th>
</tr>
</thead>
</table>

Revision Date:  2013-03-28
Reason for revision:  (M)SDS sections updated. 11. 12.

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Prepared By
Product Stewardship

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End of Material Safety Data Sheet
Procedure for Activating Klozur® Persulfate
with Dissolvine® Iron-EDTA

Background

Klozur® Persulfate can be activated with Dissolvine® iron – EDTA (chelated iron) for the oxidative destruction of organic contaminants of concern, including PCE, TCE, DCE, vinyl chloride, BTEX, low molecular weight aromatic hydrocarbons, methyl-tert-butyl ether (MTBE), 1,4-dioxane and others.

For the iron – EDTA (FeEDTA) activation of Klozur Persulfate, the iron concentration in the groundwater needs to be maintained between 150 mg / L (ppm) and 600 mg / L (ppm). Iron concentrations below 150 ppm will result in kinetics that may not be favorable for the oxidation of various contaminants, and concentrations in excess of 600 ppm may lead to increased persulfate auto-decomposition. Dissolvine Iron – EDTA is 13% iron by weight, thus requiring between 1,154 ppm and 4,615 ppm FeEDTA to maintain the desired groundwater iron concentrations.

FMC recommends the addition of FeEDTA as an activator when iron activation is selected, even if there is iron already present in the sub-surface. Measured iron concentrations present in soils may not be available for persulfate activation or the iron may not be distributed evenly enough through the treatment zone to insure adequate activation of the persulfate.

Safety and Handling

Dissolvine FeEDTA is a yellowish-green powder with slight health hazards. Appropriate Personal Protective Equipment (PPE), including chemical goggles is required when handling this product. Review the MSDS with all workers prior to handling this chemical.

FMC does not recommend combining FeEDTA with persulfate in the same batching tank, as persulfate decomposition may occur with subsequent generation of heat and oxidant loss.

Procedure for determining the amount of FeEDTA needed:

1. Determine the volume of groundwater to be treated with Fe-EDTA activated persulfate.

2. The minimum amount of FeEDTA needed to achieve 150 ppm of Fe in the groundwater can be determined by:

   \[ \text{Lbs FeEDTA} = \# \text{ gallons of groundwater} \times 150 \times 6.38 \times 10^{-5} \]
INVESTIGATION OF CHLORINATED METHANES TREATABILITY USING ACTIVATED SODIUM PERSULFATE

Duane K. Root, Ph.D. and Ellen M. Lay (Shaw Environmental, Inc., Knoxville, TN, USA)
Philip A. Block, Ph.D. and William G. Cutler, MS, RG (FMC Corporation, Philadelphia, PA, USA)

ABSTRACT: In situ chemical oxidation is a frequently used remedial approach for the destruction of chlorinated ethenes such as tetrachloroethene (PCE) and trichloroethene (TCE). However, treatment of more recalcitrant chloroethanes and chloromethanes have challenged traditional oxidation reagents. Recently, new methods of sodium persulfate reagent activation have been developed and these systems have shown promise for improved treatment performance. The new methods of persulfate activation use chelated metals, such as iron (II) ethylenediamine tetraacetic acid [Fe⁺²(EDTA)], hydrogen peroxide addition or alkaline conditions by addition of base. Both the mixed persulfate/peroxide and the alkaline persulfate reagent systems have shown the ability to treat the more recalcitrant chlorinated methanes and ethanes.

In this study the new methods of persulfate activation have been investigated in bench tests on soil/water mixtures from a site with carbon tetrachloride (CT) and chloroform (CF) contamination. The oxidant systems that were tested included persulfate activated with EDTA chelated iron (II), persulfate and hydrogen peroxide mixtures at mole ratios of 10:1, 1:1 and 1:10 and persulfate at a pH of 11-12 using base addition. The tests were designed to monitor reagent behavior in soil/groundwater mixtures as well as CT and CF treatment effectiveness.

INTRODUCTION

Persulfate ion (S₂O₈⁻²) is a strong oxidant capable of oxidizing most organic compounds to carbon dioxide and other mineral products. The standard reduction potential for the half reaction shown below is +2.01 Volts (V). It is on the same order as that for ozone and higher than that for permanganate and hydrogen peroxide, but less than that for the hydroxyl radical (OH⁻), which is a Fenton’s Reagent intermediate.

\[ \text{S}_2\text{O}_8^{2-} + 2\text{e}^- \rightarrow 2\text{SO}_4^{2-} \quad \text{E}^\circ = +2.01 \text{ V} \] (1)

It is believed that persulfate reacts with organic compounds primarily by the sulfate anion radical, which can be generated in solution by several mechanisms. The sulfate anion radical is a powerful oxidizing species with a standard electrode reduction potential of +2.6 V, which is similar to that for the hydroxyl radical (OH⁻) species (+2.8 V). The persulfate anion radical in contrast has a longer lifetime in solution and is more selective in its reactions (P. Neta,
1987).

\[
\text{SO}_4^{--} + e^- \rightarrow \text{SO}_4^{2--} \quad E^o = +2.6 \text{ V} \quad (2)
\]

Recently, new methods of persulfate reaction activation with chelated metals, such as iron (II) ethylenediamine tetraacetic acid [Fe$^{2+}$(EDTA)], hydrogen peroxide addition or alkaline conditions (pH=11-13) by addition of base have been developed (P. Block, 2004). These new methods have shown promise for in situ treatment of more recalcitrant chloroethane and chloromethane compounds and were investigated on soil/groundwater mixtures from a site with CT and CF contamination.

**MATERIALS AND METHODS**

**Soil Oxidant Demand (SOD) Tests.** Tests were performed to measure the amount of oxidant consumed in the course of treatment to destroy the target CT and CF compounds. The amount and rate of oxidant consumption is used to determine oxidant dosing and reaction condition requirements for treatment.

Tests were performed using soil/groundwater slurries with a soil to water weight ratio of 1:1.5. Persulfate oxidant systems were tested using an oxidant concentration of 22 g/L. Three molar ratios of persulfate to peroxide were tested for activation of the persulfate and the ratios were 1:10, 1:1 and 10:1. Alkaline activation of persulfate was tested at a pH of 11-12. The pH was established using sodium hydroxide addition and the dose was determined from buffering capacity measurements performed during characterization. For chelated metal activation the iron (II) EDTA complex, [Fe$^{2+}$(EDTA)] was studied. These tests used an iron concentration of 200 mg/L. Data from these tests were compared to results from similar tests using modified Fenton’s Reagent and permanganate.

**Treatment Effectiveness Tests.** Treatment tests were used to evaluate VOC treatment effectiveness over a six-week treatment period. Tests were prepared with zero headspace using 30 grams of soil and 145 milliliter (mL) of groundwater in 160 mL septum bottles for each test condition. Each test bottle was spiked with CT and CF to a target aqueous concentration of 250 mg/L of CT and 50 mg/L of CF to provide the desired concentrations for testing. Four sampling points, 3, 9, 19 and 47 days, were used to collect samples for analysis. Control tests without added oxidant were also run in parallel as a baseline to assess treatment effects due to differences in VOC concentrations.

A 1:1 molar ratio of persulfate to peroxide was tested for peroxide activation at a persulfate concentration of 4 g/L. A lower concentration was used to minimize gas evolution so the test could be performed in a sealed septum vial. Alkaline activation of persulfate was tested at a pH of 11-12 at a persulfate concentration of 22 g/L. The pH was established using trisodium phosphate (Na$_3$PO$_4$) addition to a concentration of 46 g/L, which produced pHs measuring from 11.46 to 12.11 during the test. For chelated metal activation the persulfate concentration was 22 g/L and the Fe$^{2+}$(EDTA)] complex was used at an iron
RESULTS AND DISCUSSION

Soil Oxidant Demand Results. The peroxide activated persulfate tests showed rapid consumption of both reagents in the presence of site soil. The reagents were consumed at a ratio of between 0.55 to 10 moles of hydrogen peroxide per mole of persulfate until depletion of one or both of the reagents depending on the starting concentrations. For the 10:1 peroxide to persulfate mole ratio test both reagents were essentially depleted within 24 hours. For the 1:1 mole ratio test the peroxide was consumed within 24 hours, but there was a residual persulfate concentration that was relatively stable in the absence of peroxide. For the 1:10 mole ratio test the residual persulfate was stable once the peroxide was consumed. The rapid consumption of reagent for these tests was repeated with consistency over several re-dosings, suggesting that it was due more to reagent decomposition processes than to oxidation of contaminants or soil material.

Three tests, namely the test using persulfate without activation, the alkaline persulfate test and the Fe$^{+2}$(EDTA) complex activated persulfate test were more stable toward persulfate consumption than the peroxide activated persulfate tests. Table 1 shows the initial rates of reagent consumption for these tests assuming a linear relationship with time.

<table>
<thead>
<tr>
<th>Test Description</th>
<th>Persulfate Consumption Rate $(\text{mg/L/day})$</th>
</tr>
</thead>
<tbody>
<tr>
<td>No activation</td>
<td>185</td>
</tr>
<tr>
<td>200 mg Fe$^{+2}$/L as Fe(EDTA)</td>
<td>383</td>
</tr>
<tr>
<td>pH=11-12 using NaOH</td>
<td>515</td>
</tr>
</tbody>
</table>

**Table 1. Summary of persulfate initial consumption rates in SOD tests using 22 g/L sodium persulfate and 1:1.5 soil to groundwater.**

Treatment Effectiveness Test Results. Plots of aqueous CT concentration as a function of time (days) for the soil/groundwater treatment tests are shown in Figure 1. The data show that alkaline activated persulfate was most effective in reducing CT concentrations. At the 47-day sampling point the aqueous CT concentration was reduced to 0.051 mg/L. The next most effective treatment based on residual concentration was the Fe$^{+2}$(EDTA) activated persulfate reagent, which reduced the CT concentration to 62.8 mg/L at day 47. The peroxide activated persulfate reagent was not as effective, but the peroxide dose was approximately one-fifth of the other tests. The 47-day CT concentration for this test was 119 mg/L.
Both the alkaline activated persulfate test and the Fe$^{+2}$(EDTA) activated persulfate test retained approximately 50 percent of the persulfate reagent to potentially continue treatment beyond the 47 day time point. The persulfate concentration for the peroxide activated test was less than that for the other tests and by the 9-day sampling point all of the peroxide and 75 percent of the persulfate had been consumed and there was only modest change in CT concentration beyond that point. A plot of CT concentration as a function of persulfate used is shown in Figure 2. This shows that hydrogen peroxide activated persulfate was nearly as effective as the alkaline activated persulfate for treating CT based on the amount of oxidant used, but the rapid consumption of reagent would likely make effective utilization difficult.

Plots of CF concentration as a function of time (days) for the treatment tests are shown in Figure 3. The data show that both the alkaline control and the alkaline activated persulfate tests had a reduction in aqueous CF concentration. The alkaline control had an approximate 80 percent reduction to 9.88 mg/L and the alkaline persulfate test was reduced nearly 90 percent to 5.18 mg/L. The reduction in the control CF concentration is believed to be due to alkaline hydrolysis and this may have also contributed to the reduction in the alkaline activated persulfate test. Chloroform is more readily hydrolyzed by base than either CT or methylene chloride (J. March, 1968). The other tests did not indicate a significant change in CF concentration.
Figure 2. Aqueous carbon tetrachloride concentration in treatment systems as a function of persulfate used

Figure 3. Chloroform treatment results in soil/groundwater mixtures for activated persulfate systems
CONCLUSIONS

Activated persulfate systems demonstrated the ability to treat CT concentrations in soil/groundwater mixtures. Persulfate activated by alkaline conditions demonstrated the best performance in reducing aqueous CT concentrations as well as providing the greatest reduction for the amount of oxidant used. Peroxide and Fe$^{2+}$(EDTA) activated persulfate systems also provided reductions in concentration, but not to the same extent as the alkaline activated persulfate.

Alkaline conditions both for the persulfate control test and the persulfate treatment test provided a reduction in CF concentrations with the persulfate treatment providing a slightly lower residual CF concentration. The reduction in control CF concentration was attributed to alkaline hydrolysis of CF, which most likely also contributed to the reduction observed in the persulfate treatment test. Neither the peroxide activated persulfate nor the Fe$^{2+}$(EDTA) activated persulfate systems provided significant treatment.

Peroxide activated persulfate systems were not stable in the presence of site soil. The reagents were typically consumed within 24 hours at rates of 0.5 to 10 moles of peroxide per mole of persulfate until peroxide was depleted and then residual persulfate concentrations were relatively stable. In the absence of site soil the reagent combination was more stable losing less than 50 percent of their concentrations over three weeks.

REFERENCES


Applying Klozur persulfate solution and FeEDTA activator to a contaminated site

Various combinations of Klozur persulfate and FeEDTA in solution may undergo an exothermic reaction, potentially leading to significant heat generation (with temperature increases to 100 C possible) and oxidant loss. As a result:

**FMC does not recommend combining FeEDTA with persulfate in the same batching tank.**

Instead, it is recommended that separate batch tanks be utilized to make up the persulfate solution and the FeEDTA solution. The solutions may then be mixed prior to the well-head and co-injected or injected separately in a serial fashion.

At room temperature, FeEDTA is soluble at a concentration of 0.75 lb / gallon.
Bench-Scale Treatability Study
TREATMENT OF FREON AND CHLORINATED HYDROCARBONS
USING VERUTEK’S S-ISCO™ COELUTION TECHNOLOGY™

Groundwater samples were collected from a former industrial manufacturing facility with moderate FREON-113 and chlorinated hydrocarbon contamination. These samples were characterized to determine initial FREON-113 and other volatile compound contamination levels prior to using in three laboratory tests:

- Test 1: No treatment (control)
- Test 2: Alkaline persulfate
- Test 3: Fe-EDTA Catalyzed Persulfate

Each test contained the same amount of groundwater. Each test also contained approximately the same amount of contaminants initially; the table and graph below demonstrate the effectiveness of S-ISCO™ in destroying FREON-113 and chlorinated hydrocarbon contamination after 5 days:

<table>
<thead>
<tr>
<th>Volatile Organic Compound (VOC) Concentrations (μg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>VOC (μg/L)</td>
</tr>
<tr>
<td>FREON-113</td>
</tr>
<tr>
<td>1,1,1-Trichloroethane</td>
</tr>
<tr>
<td>1,1-Dichloroethane</td>
</tr>
<tr>
<td>1,1-Dichloroethene</td>
</tr>
<tr>
<td>Chloromethane</td>
</tr>
<tr>
<td>cis-1,2-Dichloroethene</td>
</tr>
<tr>
<td>Tetrachloroethene</td>
</tr>
<tr>
<td>Trichloroethene</td>
</tr>
<tr>
<td>Total VOCs</td>
</tr>
</tbody>
</table>

ND – Non Detect
* Common Laboratory Contaminant

VOC Concentrations

Treatment with S-ISCO™ using Alkaline Activated Persulfate technology led to the destruction of 100% of the FREON-113 and chlorinated hydrocarbon contamination in just 5 days.

www.VeruTEK.com
Case Study: Fayette County, Georgia

Updated: August 2008

Description:
Active Gasoline station. Petroleum constituents in the groundwater due to off-site migration. Plume size was approximately 360 feet in length by 60 feet in width. Geology of Study Area: Piedmont saprolite (sandy silts, silty-sands, heterogeneous). Depth to groundwater ranged from one-foot below ground surface (bgs) to approximately 25 foot bgs.

Contaminant: Benzene max. contamination 18,000 µg/L in groundwater.

Treatment goal:
To reduce BTEX constituents in groundwater to below In-Stream Water Quality Standards (ISWQS) or Alternative Contaminant Levels (ACLs) for the known area of contamination

Treatment approach:
Initially, a pilot test utilizing a mobile Dual-Phase Extraction (DPE) system was implemented at this facility with limited effectiveness due to low permeability soils. Exo Tech, Inc. conducted a treatibility study using sodium persulfate activated with in-situ iron; hydrogen peroxide, and chelated iron (FeEDTA). Results of the Treatability Study indicated sodium perfsulfate activated with FeEDTA resulted in complete oxidation of petroleum constituents and allowed for a more extended subsurface reaction.


Total number of wells injected: 99

Sampling time line:
- 9/13/07 Pre-injection sampling of all wells
- 2/21/08 Pre-injection sampling of most wells
- 5/8/08 Pre-injection sampling of most wells

Results:
Significant reduction in dissolved benzene/total BTEX was observed throughout the plume based on confirmation sampling. Further results pending.

Sampling schedule:
The first post-injection sampling event occurred 37 days after the injection and revealed that the well previously observed to be the most contaminated showed a 78% reduction of benzene from 22,000 ug/l in April 2007 to 1,200 ug/l approximately 37 days after the injection. In summary, significant reductions of BTEX in groundwater were observed as early as 37 days post-injection.

Site Status:
Currently completing remediation as directed by the GA EPD.

Project cost: $197,676
**Abstract**

Methyl tert Butyl Ether (MTBE) is a gasoline additive that was required in many states to reduce ozone and carbon monoxide emissions in automobile exhaust. However, in states where MTBE was widely used, its use resulted in widespread groundwater contamination. Based on a 2000 US Geological Survey, 20% of the nation’s drinking water supply may have MTBE contamination. The project has recently finished the treatability phase, and the results are shown at the left. The activation chemistry chosen was Fe-EDTA. The results demonstrate that activated persulfate can readily destroy MTBE. The effect of persulfate and Fe-EDTA concentration on the kinetics of MTBE destruction is seen in the data. At the higher concentrations, the MTBE concentration was reduced by 99% within one week.

Redox Tech has had success in implementing Klozur® peroxulfate in the field with steam and alkaline activation to treat MTBE. Field data is shown on the right, demonstrating that MTBE contamination can be reduced by up to 99%.

**In Situ Treatment of Groundwater with Klozur® Activated Persulfate**

Klozur® peroxulfate is one of the strongest oxidants available for environmental remediation. The standard oxidation – reduction potential for the reaction

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

is 2.1 V, as compared to 1.8 V for hydrogen peroxide (H2O2) and 1.4 V for the peroxynitrous acid (HONO). This potential is also higher than the redox potential for the permanganate anion (MnO4-) at 1.7 V, but slightly lower than that of ozone at 2.2 V.

However, for most contaminants, the kinetic of direct oxidation by peroxulfate anions are too slow. Peroxulfate can be induced to form sulfate radicals, thereby providing free radical reaction mechanisms, similar to the hydroxyl radical pathways generated by Fenton’s chemistry. The generation of sulfate radicals is

\[ \text{S}_2\text{O}_8^{2-} \rightarrow 2\text{SO}_4^{2-} \text{ or } (\text{SO}_4^{\bullet} + \text{SO}_4^-) \]

The sulfate radical is one of the strongest aqueous oxidizing species with a redox potential estimated as 2.6 V, which is similar to the hydroxyl radical at 2.7 V. Several methods are available to activate peroxulfates. These include heat and several FMC patented pending chemistries such as alkali, chlorinated metals, and hydrogen peroxide.

**Laboratory Investigation**

The ability of activated persulfate to destroy MTBE was investigated in the laboratory. Klozur® peroxulfate was dosed at 1.5 times the stoichiometric quantity needed to fully mineralize the MTBE. Activator systems were dosed as described. Analysis was performed using GC-MS. It is observed from the results, that the oxidative destruction proceeds through the formation of intermediate daughter products such as tert-butyl alcohol (TBA) and acetone. The rate of destruction of the MTBE, and its daughter products, is dependent upon the activation chemistry utilized, temperature, and concentration of persulfate and activator.

**OHP® Laboratory Demonstration**

Groundwater samples taken from an MTBE-contaminated aquifer in Long Island, NY were utilized for a laboratory demonstration of the OHP® process efficiency. A laboratory scale version of reactor system was utilized. The groundwater sample had a TOC of 125 mg/L. Two different temperatures and ratios of hydrogen peroxide to TOC were investigated: 250 gm peroxide per gm TOC at 115°C and 125 gm peroxide per gm TOC at 80°C. 0.1 g of FeSO4•7H2O was used per 100 ml of sample. The pH for both conditions was 3.4 with a reaction time of 30 minutes. No further process optimization was performed. MTBE concentration was determined by SPEX extraction followed by GC analysis.

**Ex Situ Treatment of Groundwater with the OHP® Process**

MTBE can successfully be treated with chemical oxidation. Groundwater can readily be treated in situ with Klozur® activated persulfate. The rate of MTBE destruction, as well as TBA and acetone intermediates, can be controlled by choice of activator (heat, peroxide, alkaline or Fe-EDTA) and concentration of the oxidant. Treatment of groundwater streams as ex situ can be accomplished with the OHP® process, a “continuous” batch reactor system, in a cost effective manner.

**Conclusions**

MTBE is a potent process to treat organic waste via a chemical oxidation. The process generates hydroxyl radicals as well as MTBE destruction, as well as TBA and acetone intermediates, can be controlled by choice of activator (heat, peroxide, alkaline or Fe-EDTA) and concentration of the oxidant. Treatment of groundwater streams as ex situ can be accomplished with the OHP® process, a “continuous” batch reactor system, in a cost effective manner.
Case Study Comparison of Multiple Activation Methods for Sodium Persulfate Treatment

Gary Cronk, P.E., CHMM
JAG Consulting Group, Inc.
Santa Ana, CA

ORTs-6 Conference, San Diego, CA
September 23, 2008
Introduction to Persulfate Activation

- To obtain optimal treatment results, must select proper activator for persulfate
- Dependent upon the contaminant of concern and the specific site conditions
- Activation Methods for Persulfate include:
  - Hydrogen Peroxide
  - High pH (pH over 10.5) (Alkaline Activation)
  - Chelated Iron (EDTA) or Ferrous Iron
  - Heat
Considerations in Selecting an Activator

- Most aggressive activators are Hydrogen Peroxide and high pH
- A wide variety of VOCs can be treated, including many recalcitrant compounds such as DCA, TCA, vinyl chloride, PCBs, & PAHs
- However, potential for adverse reactions and sensitive site conditions may limit use of peroxide and high pH
- Iron activation is **not** recommended for treatment of gasoline, diesel fuel, Freon, PCBs, TCA, DCA, vinyl chloride, or pesticides
- A Treatability Test should be performed to confirm treatment efficiency and determine site specific Soil Oxidant Demand
Considerations in Selecting an Activator

- Sites with shallow groundwater table are prone to “daylighting” of peroxide
- Potential for corrosion or damage to metal pipes, utilities, and other sensitive areas (peroxide and high pH)
- Adequate venting of off-gases are critical to prevent bulging of pavement and other serious damage (peroxide)
- Due to safety concerns, the RWQCB has recently limited the concentration of peroxide to 10% and the maximum temperature increase to 150 degree F
When Should Persulfate Oxidation Be Used?

- Need for Fast Site Cleanup
- Need for Economical Site Cleanup
- Focused Hot Spot Treatment
- To Expedite “Past Due” Pump & Treat Systems
Case Study 1: Peroxide Activation
Rancho Dominguez, CA

• 23 Injection Wells - Mostly Inside an Occupied Industrial Building
• Created Hydraulic Barrier
• Injected 16,000 lbs of Persulfate
• Injected 12,000 gals of Peroxide
• After 120 days, Attained Reductions of 94% to 99% in Methylene Chloride Levels
• Recently received Closure from LARWQCB
• Project Performed by MECX and Tait Environmental in 2005
Case Study 1: Peroxide Activation
Rancho Dominguez, CA

[Graph showing concentration (ug/l) over days for MW-1A, MW-9A, MW-11, MW-12]
Case Study 2: Peroxide Activation
La Mirada, CA

- Primary contaminant is Benzene
- Six Injection Wells
- Injected 14,000 lbs Persulfate
- Injected 7,200 gal peroxide
- Permeable Sands and Silts
- 18 ft Radius of Influence
- Project Performed by MECX and JAG Consulting in 2006
Case Study 2: Peroxide Activation
La Mirada, CA

Dissolved Benzene Reductions Following ISCO Treatment

Day 0
1st ISCO Application
Persulfate and Peroxide

Day 166
2nd ISCO Application
Persulfate Only
Case Study 3: High pH (Alkaline) Activation
Santa Ana, CA

- Site Contaminated with TCE, 1,1-DCE, 1,1,1-TCA, and other VOCs
- Two Injection Wells (Pilot Test)
- Injected 3,000 lbs of Persulfate
- Injected 600 gals of 25% Sodium Hydroxide
- Achieved Immediate DCE reductions of 90%-100%
- DCE rebound After 60 days
- Project Performed by MECX and URS Corporation in 2006
Case Study 3: High pH Activation
Santa Ana, CA

Days Following ISCO
1,1-DCE (ug/L)

Well 1A
Well 1B
Well 2
Case Study 4: High pH (Alkaline) Activation
Huntington Harbor, CA

- UST Site Contaminated with TPH Gas, BTEX, and MTBE
- Three well Pilot Test
- Injected 3,000 lbs of Persulfate
- Injected 2,900 gals of 25% Sodium Hydroxide

- Reduced TPH gas, BTEX, and MTBE Levels by 78% to 100%
- Project Performed by JAG Consulting and Tait Environmental
Case Study 4: High pH Activation
Huntington Harbor, CA

TPH Gas Reductions in Monitoring Wells

BTEX Reductions in Monitoring Wells

MW-2
MW-10
Case Study 5: Ferrous Sulfate Activation
La Mirada, CA

• Benzene Levels Rebounded after Peroxide Activated Persulfate Treatment
• Two Injection Wells
• Injected 7,000 lbs of persulfate
• Injected 600 pounds of ferrous sulfate

• 2nd ISCO application reduced benzene levels by 94%
• Project Performed by JAG Consulting in 2007
Case Study 5: Benzene Reductions Using Ferrous Sulfate Activation
La Mirada, CA

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### Benzene Levels (ug/l) over Time

<table>
<thead>
<tr>
<th>Day</th>
<th>Well MW-4</th>
<th>Well GTI-14</th>
</tr>
</thead>
<tbody>
<tr>
<td>Day 0</td>
<td>470</td>
<td>2,900</td>
</tr>
<tr>
<td>Day 15</td>
<td>250</td>
<td>800</td>
</tr>
<tr>
<td>Day 22</td>
<td>0</td>
<td>450</td>
</tr>
<tr>
<td>Day 25</td>
<td>0</td>
<td>1,000</td>
</tr>
<tr>
<td>Day 45</td>
<td>8</td>
<td>520</td>
</tr>
<tr>
<td>Day 60</td>
<td>150</td>
<td>380</td>
</tr>
<tr>
<td>Day 199</td>
<td>140</td>
<td>66</td>
</tr>
<tr>
<td>Day 253</td>
<td>160</td>
<td>26</td>
</tr>
</tbody>
</table>
Case Study 6: Iron EDTA Activation
La Mirada, CA

- Treatment of TCE Plume
- Three Injection Wells
- Injected 6,700 lbs of persulfate
- Injected 1,500 pounds of iron EDTA
- Project Performed by JAG Consulting in 2008
Conclusions & Lessons Learned

- Good to excellent contaminant reductions achieved using all activation methods for Persulfate
- Selection of the Activator should be based on Contaminant of Concern and Site Conditions
- Pilot Tests should include a minimum of 3 wells and be located in an up-gradient area (near source)
- Multiple Monitoring Wells Should be located Nearby
- Received Closure of Three Sites in California to Date