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

MSDS #: 15708-41-5
Revision Date: 2013-03-28
Version 1

This MSDS has been prepared to meet U.S. OSHA Hazard Communication Standard 29 CFR 1910.1200
and Canada's Workplace Hazardous Materials Information System (WHMIS) requirements.

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1. PRODUCT AND COMPANY IDENTIFICATION

Product name	**Dissolvine® E-FE-13**
Synonyms	Ferric sodium EDTA; CHEMICAL NAME: Ethyldiaminetetraacetic acid, ferric sodium complex
Formula	$C_{10}H_{12}FeN_2O_8Na.3H_2O$
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

Ingredients

Chemical Name	CAS-No	Weight %
EDTA ferric sodium complex	15708-41-5	87-89
Water	7732-18-5	11-13

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.

NFPA	**Health Hazard** 1	**Flammability** 1	**Stability** 0	**Special Hazards** -

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 .

Chemical Name	ACGIH TLV	OSHA PEL	NIOSH	Mexico
EDTA ferric sodium complex 15708-41-5	TWA: 1 mg/m³		TWA: 1 mg/m³	
Chemical Name	**British Columbia**	**Quebec**	**Ontario TWAEV**	**Alberta**
EDTA ferric sodium complex 15708-41-5	TWA: 1 mg/m³ STEL: 2 mg/m³	TWA: 1.0 mg/m³		TWA: 1 mg/m³

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

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

9.2 Other information

Autoignition Temperature	> 200 °C

10. Stability and reactivity

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

11. Toxicological information

Acute effects

Eye irritation	Non-irritating.
Skin irritation	Non-irritating to the skin
LD50 Oral	> 2000 mg/kg bw (rat)
LD50 Dermal	> 2000 mg/kg bw (rat)
LC50 Inhalation:	> 2.75 mg/L (4-hr)
Sensitization	Did not cause sensitization on laboratory animals.

Chronic Toxicity

Chronic Toxicity	In a 31/61-day oral study on rats with Ferric-sodium EDTA, the NOAEL >/= 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 Lynphoma 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)

Active Ingredient(s)	Duration	Species	Value	Units:
Ferric Sodium EDTA	96 h LC50	Rainbow trout	>100	mg/L
Ferric Sodium EDTA	35 day NOEC.	Zebra fish	28.9	mg/L
Ferric Sodium EDTA	48 h EC50	Daphnia magna	100.9	mg/L
Ferric Sodium EDTA	21 day NOEC.	Daphnia magna	31	mg/L
Ferric Sodium EDTA	72 h NOEC	Algae	69.9	mg/L

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.

Chemical Name	log Pow
EDTA ferric sodium complex	-10.6 (based on EPIWN model)

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

DOT	not regulated
TDG	not regulated
ICAO/IATA	not regulated
IMDG/IMO	not regulated

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

HMIS	Health Hazard 1	Flammability 1	Stability 0	Special precautions -

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

Disclaimer

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Prepared By

Product Stewardship

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FMC Logo - Trademark of FMC Corporation

End of Material Safety Data Sheet

FMC
Environmental Solutions

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. Dissovline 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:

$$\text{Lbs FeEDTA} = \text{\# gallons of groundwater} * 150 * 6.38 \times 10^{-5}$$

Preprint: Proceedings of the First International Conference on Environmental Science and Technology (2005)

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 ($S_2O_8^{=}$) 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.

$$S_2O_8^{-2} + 2e^{-} \rightarrow 2SO_4^{-2} \qquad E° = +2.01\ V \qquad (1)$$

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).

$$\cdot SO_4^- \; + \; e^- \; \rightarrow \; SO_4^{-2} \qquad E^\circ = +2.6\ V \qquad (2)$$

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_3PO_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

(Fe^{+2}) concentration of 200 mg/L.

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.

Test Description	Persulfate Consumption Rate [(mg/L)/day]
No activation	185
200 mg Fe^{+2}/L as Fe(EDTA)	383
pH=11-12 using NaOH	515

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.

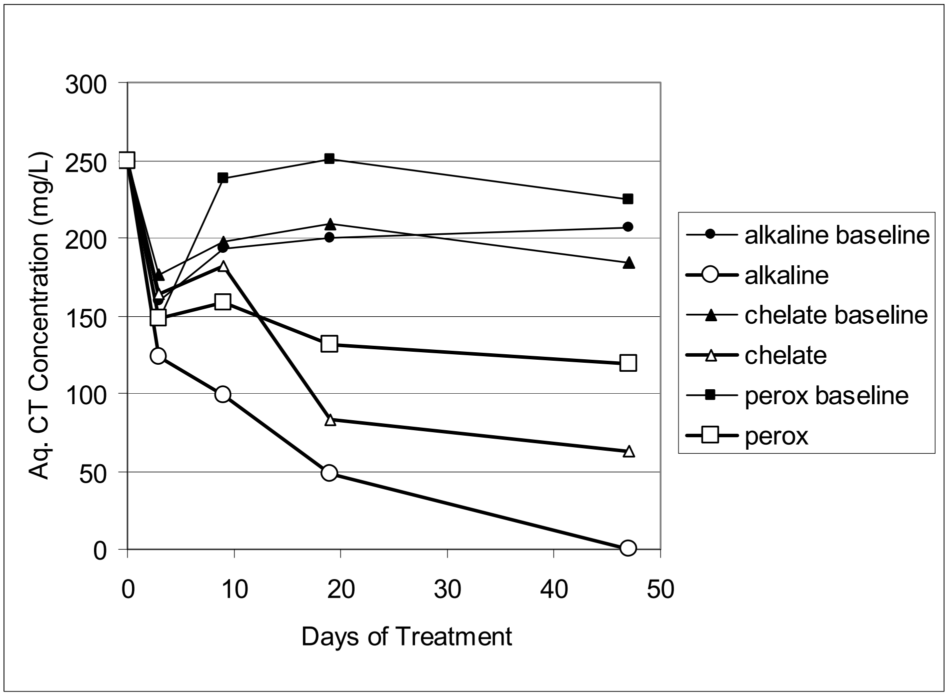


Figure 1. Carbon tetrachloride treatment results in soil/groundwater mixtures for activated persulfate systems

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.

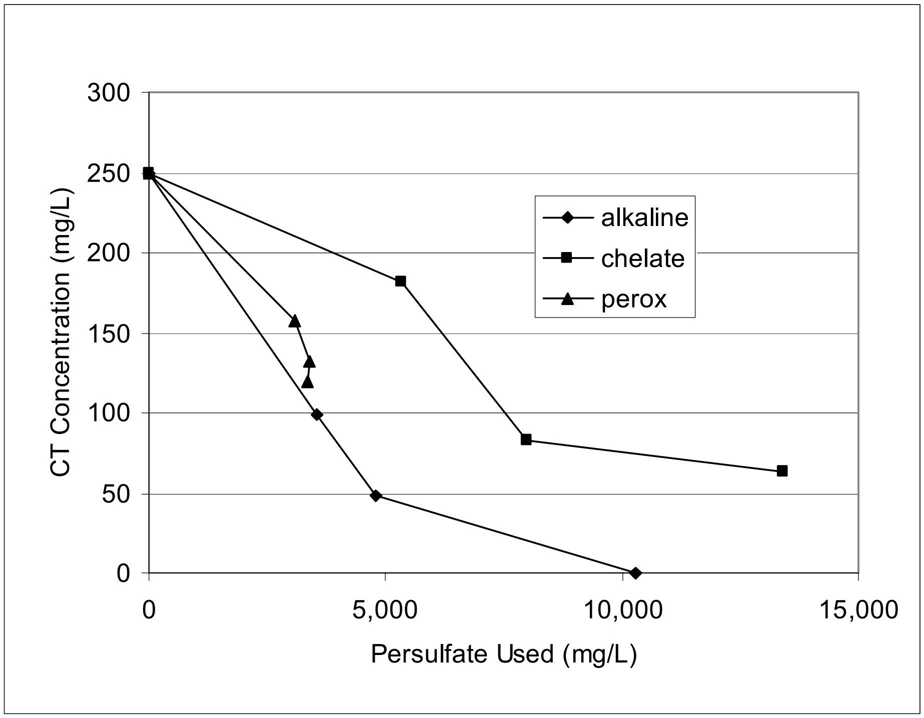


Figure 2. Aqueous carbon tetrachloride concentration in treatment systems as a function of persulfate used

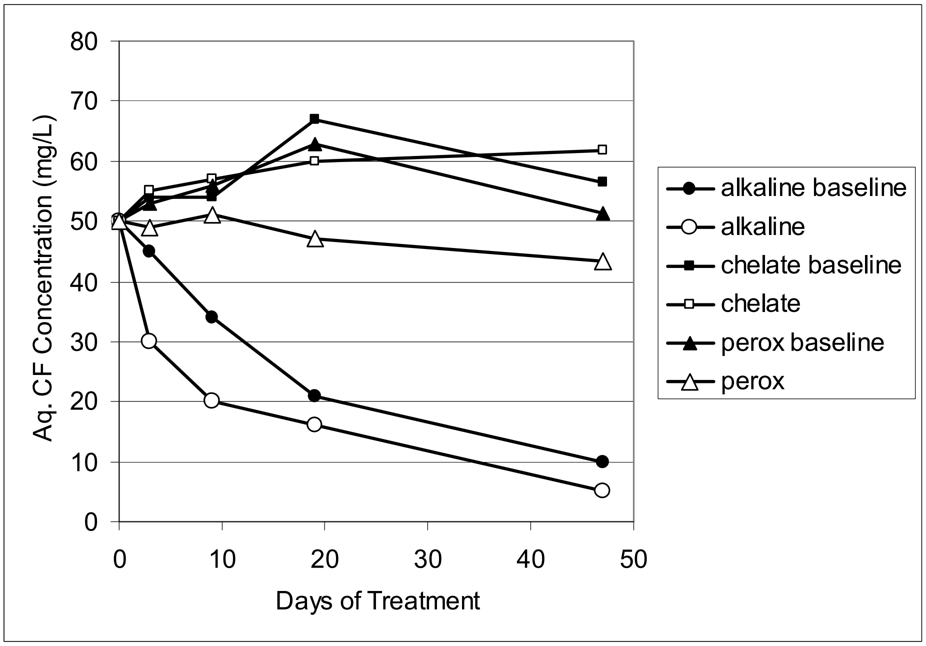


Figure 3. Chloroform treatment results in soil/groundwater mixtures for activated persulfate systems

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

Block, P. A., R. A. Brown and D. Robinson. 2004. "Novel Activation Technologies for Sodium Persulfate In Situ Chemical Oxidation." Proceedings of the Fourth International Conference on the Remediation of Chlorinated and Recalcitrant Compounds," Monterrey CA.

March, J. 1968. *Advanced Organic Chemistry: Reactions, Mechanisms and Structure.* McGraw-Hill, Inc. page 304. Reference: Hine. 1950. J. Am. Chem. Soc. 72. 2438; and le Noble. 1965. J. Am. Chem. Soc. 87. 2434.

Neta, P., R. E. Huie and A. B. Ross. 1987. *Rate Constants for Reactions of Inorganic Radicals in Aqueous Solution.* Chemical Kinetics Division, National Bureau of Standards and the University of Notre Dame Radiation Laboratory, Document No. NDRL-3028.

FMC

Environmental Solutions

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.

Document: 01-01-EIT-DI. This document is for guidance purposes only and does not guarantee freedom from injury or damage. Review all relevant MSDS's. For questions, please contact the Environmental Industry Team (EIT) at 866-860-4760.

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

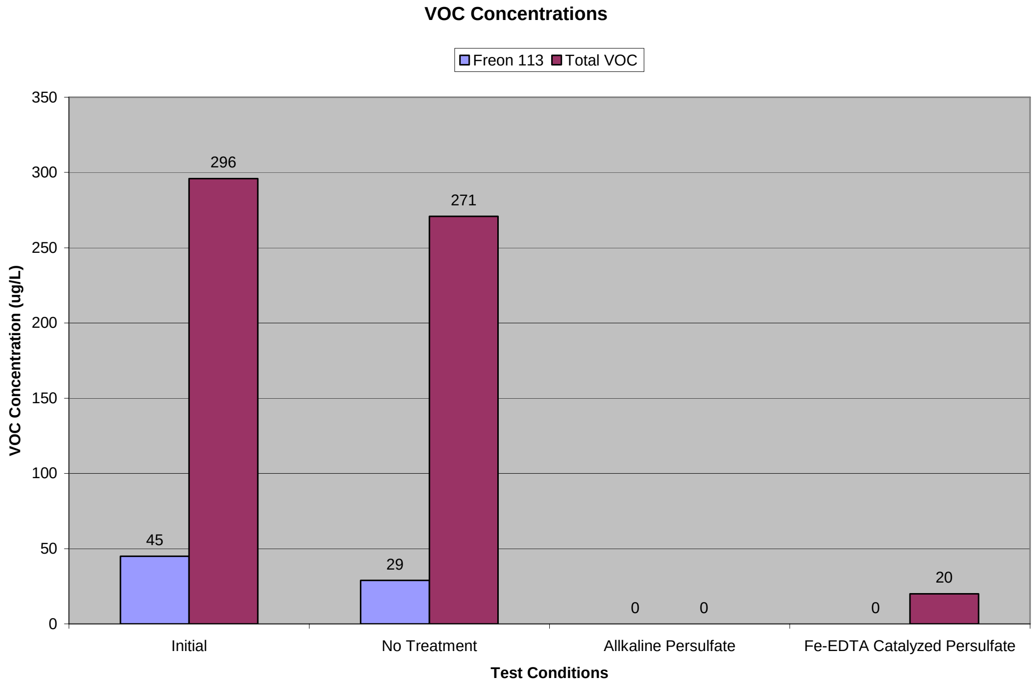
Each test contained the same amount of groundwater. Each test also contained approximately the same amount of contaminants initially; the table and graph below demonstrate the effectiveness of S-ISCO™ in destroying FREON-113 and chlorinated hydrocarbon contamination after 5 days:

Volatile Organic Compound (VOC) Concentrations (μg/L)

VOC (μg/L)	**Initial**	**Control**	**Alkaline Persulfate**	**Fe-EDTA Catalyzed Persulfate**
FREON-113	**45**	**29**	**ND**	**ND**
1,1,1-Trichloroethane	14	12	ND	ND
1,1-Dichloroethane	24	22	ND	ND
1,1-Dichloroethene	9	8	ND	ND
Chloromethane	ND	ND	ND	20*
cis-1,2-Dichloroethene	24	22	ND	ND
Tetrachloroethene	110	110	ND	ND
Trichloroethene	70	68	ND	ND
Total VOCs	**296**	**271**	**0**	**20**

ND – Non Detect

** Common Laboratory Contaminant*



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.

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.

Injection dates: 6/26-27/2006, 10/17-30/2007, and 5/19-21/2008

Total number of wells injected: 99

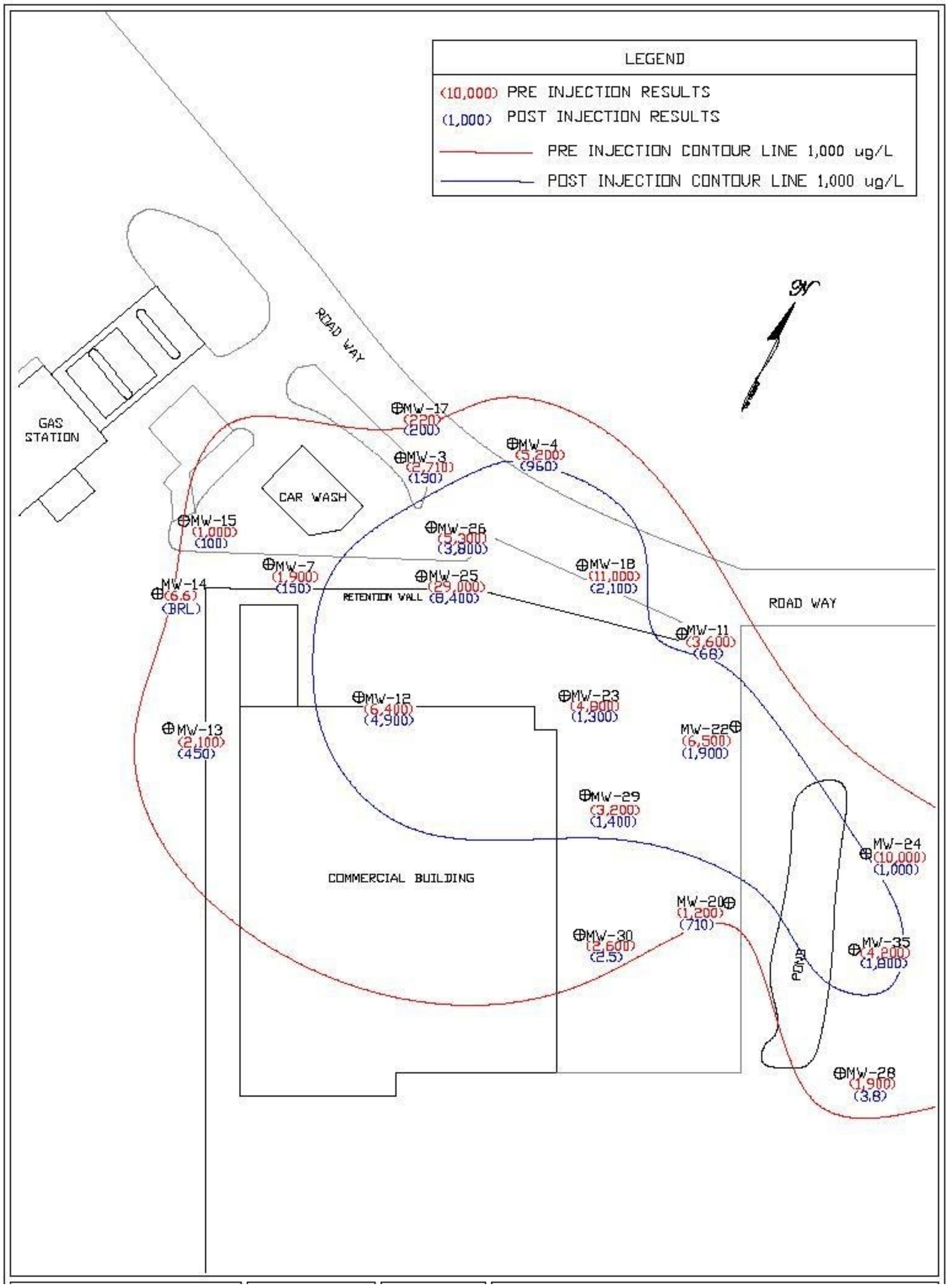
Sampling time line:
- 9/13/07 Pre-injection sampling of all wells
- 2/21/08 Pre-injection sampling of most wells
- 5/8/08 Pre-injection sampling of most wells

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


LEGEND
(10,000) PRE INJECTION RESULTS
(1,000) POST INJECTION RESULTS
PRE INJECTION CONTOUR LINE 1,000 ug/L
POST INJECTION CONTOUR LINE 1,000 ug/L
N
ROAD WAY
GAS STATION
CAR WASH
MW-17 (220) (200)
MW-3 (2,710) (130)
MW-4 (5,200) (960)
MW-15 (1,000) (100)
MW-26 (5,300) (3,800)
MW-18 (11,000) (2,100)
MW-7 (1,900) (150)
MW-25 (29,000) (8,400)
MW-14 (6.6) (BRL)
RETENTION WALL
ROAD WAY
MW-11 (3,600) (68)
MW-12 (6,400) (4,900)
MW-23 (4,800) (1,300)
MW-22 (6,500) (1,900)
MW-13 (2,100) (450)
MW-29 (3,200) (1,400)
MW-24 (10,000) (1,000)
COMMERCIAL BUILDING
MW-20 (1,200) (710)
MW-30 (2,600) (2.5)
MW-35 (4,200) (1,800)
POND
MW-28 (1,900) (3.8)

In Situ and *Ex Situ* Treatment of MTBE Contaminated Groundwater

P.A. Block, D. Sethi, S. Yuan and K. Huang
FMC Corporation

AIM:
Back to clean water

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 because of their proximity to gasoline storage tanks. MTBE has been found in samples of 1512 drinking water systems in 28 states, and 42 states have already established MTBE cleanup levels.

MTBE is readily destroyed by chemical oxidation. For *in situ* applications, Klozur^{tm} activated persulfate is used to treat MTBE-contaminated groundwater. Due to the oxidative strength of the sulfate radical, Klozur^{tm} activated persulfate is not only effective in destroying MTBE, but also BTEX and other gasoline-related contaminants, making it a very effective tool for the clean-up of gas stations. For *ex situ* applications, such as the treatment of groundwater from a pump and treat system, the OHP® process is utilized. The OHP® process is a "continuous" batch reactor which generates either the hydroxyl radical or the sulfate radical, either which is a very strong oxidant capable of completely eliminating MTBE. Optimization of the OHP® process allows for a cost effective process in treating groundwater.

In Situ Treatment of Groundwater with Klozur^{tm} Activated Persulfate

Klozur^{tm} persulfate is one of the strongest oxidants available for environmental remediation. The standard oxidation – reduction potential for the reaction

$$S_2O_8^{-2} + 2H^+ + 2e^- \rightarrow 2HSO_4^{-1}$$

is 2.1 V, as compared to 1.8 V for hydrogen peroxide (H2O2) and 1.4 V for the peroxymonosulfate anion (HSO_5^-). This potential is also higher than the redox potential for the permanganate anion (MnO_4^-) at 1.7 V, but slightly lower than that of ozone at 2.2 V.

However, for most contaminants, the kinetics of direct oxidation by persulfate anions are too slow. Persulfate 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

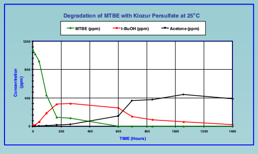
$$S_2O_8^{-2} \rightarrow 2\ SO_4\bullet \text{ or } (SO_4\bullet + SO_4^{-2})$$

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 persulfate. These include heat and several FMC patent-pending chemistries such as alkali, chelated metals, and hydrogen peroxide.

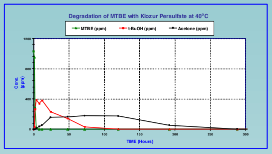
Laboratory Investigation

The ability of activated persulfate to destroy MTBE was investigated in the laboratory. Klozur^{tm} persulfate 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.

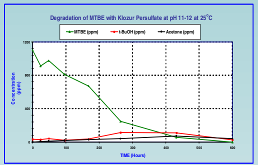
It is observed from the results, that the oxidative destruction proceeds through the formation of intermediate daughter products such as tert-butyl alcohol (TBA) and acetone. The rate of destruction of the MTBE, and its daughter products, is dependent upon the activation chemistry utilized, temperature, and concentration of persulfate and activator.



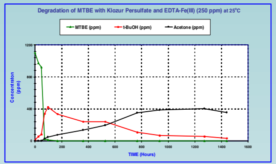
Laboratory Data for un-activated Klozur^{tm} persulfate



Laboratory Data for heat - activated Klozur^{tm} persulfate



Laboratory Data for alkaline-activated Klozur^{tm} persulfate



Laboratory Data for FeEDTA-activated Klozur^{tm} persulfate

Klozur^{tm} Treatability and Field Data

Shaw Test	Time Point (Days)	Sodium Persul Aqueous Conc. (mg/L)	Fe-EDTA Conc. mg Fe/L	MtBE (ppb)	% MTBE reduction
Control (Aq)	0	0	0	16100	
Control (Soil)	0	0	0	3200	
Control (Aq)	7	0	0	14800	
Control (Aq)	21	0	0	14300	
Control (Soil)	21	0	0	7140	
Low Trt (Aq)	7	10,000	50	12100	18.2
Low Trt (Aq)	21	10,000	50	6460	54.8
Low Trt (Soil)	21	10,000	50	3460	51.5
High Trt (Aq)	7	30,000	150	1020	93.1
High Trt (Aq)	21	30,000	150	16.6	99.9
High Trt (Soil)	21	30,000	150	ND	100.0

Data provided by D. Root and S. Abrams of Shaw E&I

Klozur^{tm} activated persulfate was utilized by Shaw E&I for treatment of a Florida gasoline station with MTBE contamination of soil and groundwater. 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^{tm} persulfate 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%.

Redox Tech, LLC Location	Contaminant (ug/L)	Pre-Injection Concentration (ug/L)	Post-Injection Concentration (ug/L)	% Reduction
Blackstone, VA	Benzene	1,600	78	95.1%
Blackstone, VA	MTBE	1,300	360	72.3%
Clayton, DE	Benzene	519	7.4	98.5%
Clayton, DE	MTBE	16,100	233	98.5%

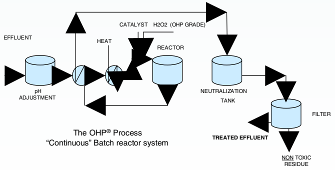
Data provided by J. Haselow of Redox Tec

Ex Situ Treatment of Groundwater with the OHP® Process

OHP® is a patented process to treat organic waste via a chemical oxidation. The process generates hydroxyl radicals as by Fenton's reaction:

$$H_2O_2 + Fe^{+2} \rightarrow OH\bullet + OH^- + Fe^{+3}$$

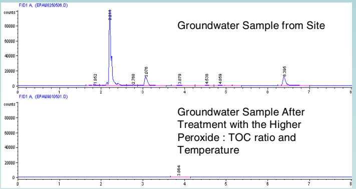
The process can be modified to generate sulfate radicals as well.



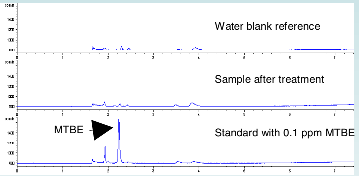
The OHP® Process
"Continuous" Batch reactor system

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 80C. 0.1 g of $FeSO_4\bullet 7H_2O$ 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 SPME extraction followed by GC analysis.



At left is displayed the data from the lab study, utilizing the higher temperature and peroxide to TOC ratio. Complete destruction of the MTBE is observed. Similar results were observed for the lower temperature and peroxide to TOC ratio study.



For comparison purposes, the treated sample GC chromatograph is displayed to the left along with a blank water sample trace and a trace from a water sample spiked with 0.1 ppm MTBE. It is clear from this figure that the groundwater is treated to clean water following the OHP® process.

Based on the lower temperature and peroxide to TOC ratio, the operating costs for treatment at full scale are estimated to be 7.4 cents per gallon of groundwater. A magnitude drop in operating cost is expected with further optimization of the peroxide level and temperature.

OHP® Pilot Process Plant

Conclusions

MTBE can successfully be treated with chemical oxidation. Groundwater can readily be treated *in situ* with Klozur^{tm} 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 FeEDTA) and concentration of the oxidant. Treatment of groundwater streams *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

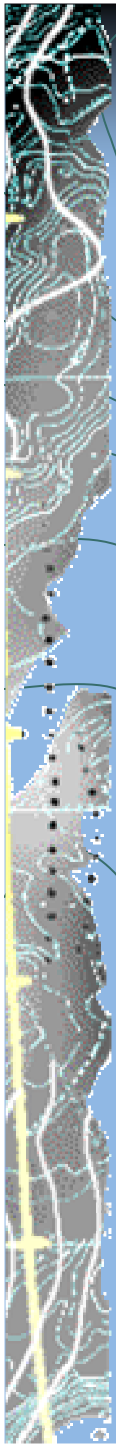
JAG Consulting Group, Inc.

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 to should be performed to confirm treatment efficiency and determine site specific Soil Oxidant Demand

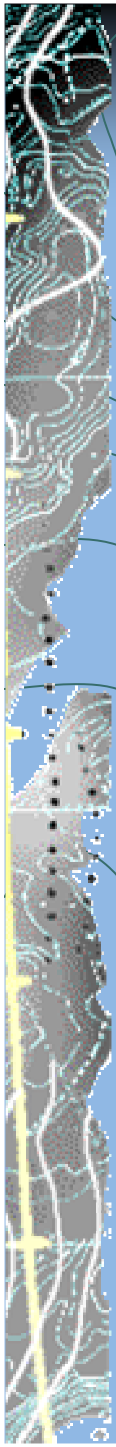
Considerations in Selecting an Activator

- 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?

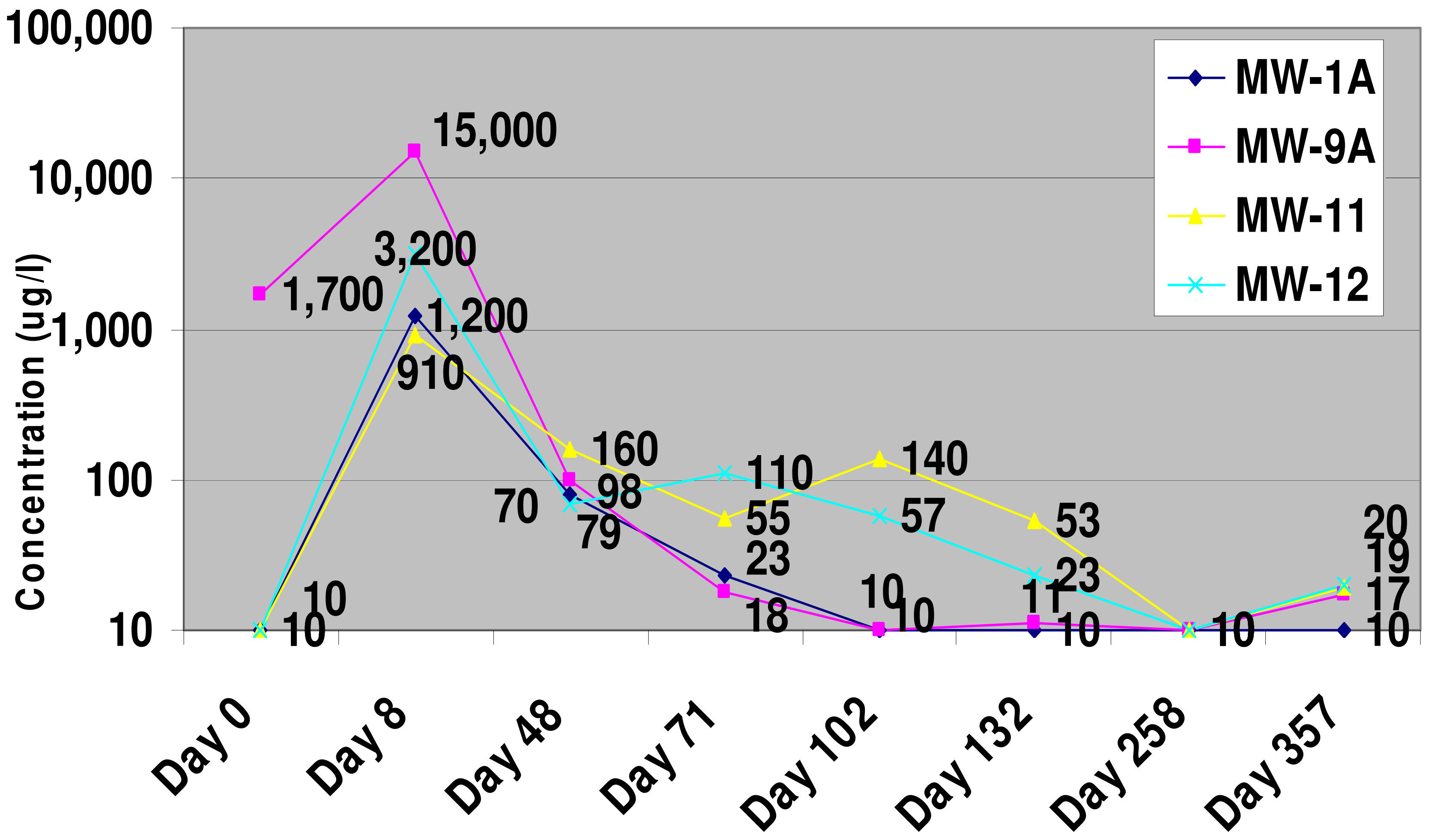
- Need for Fast Site Cleanup
- Need for Economical Site Cleanup
- Focused Hot Spot Treatment
- To Expedite “Past Due” Pump & Treat Systems



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



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

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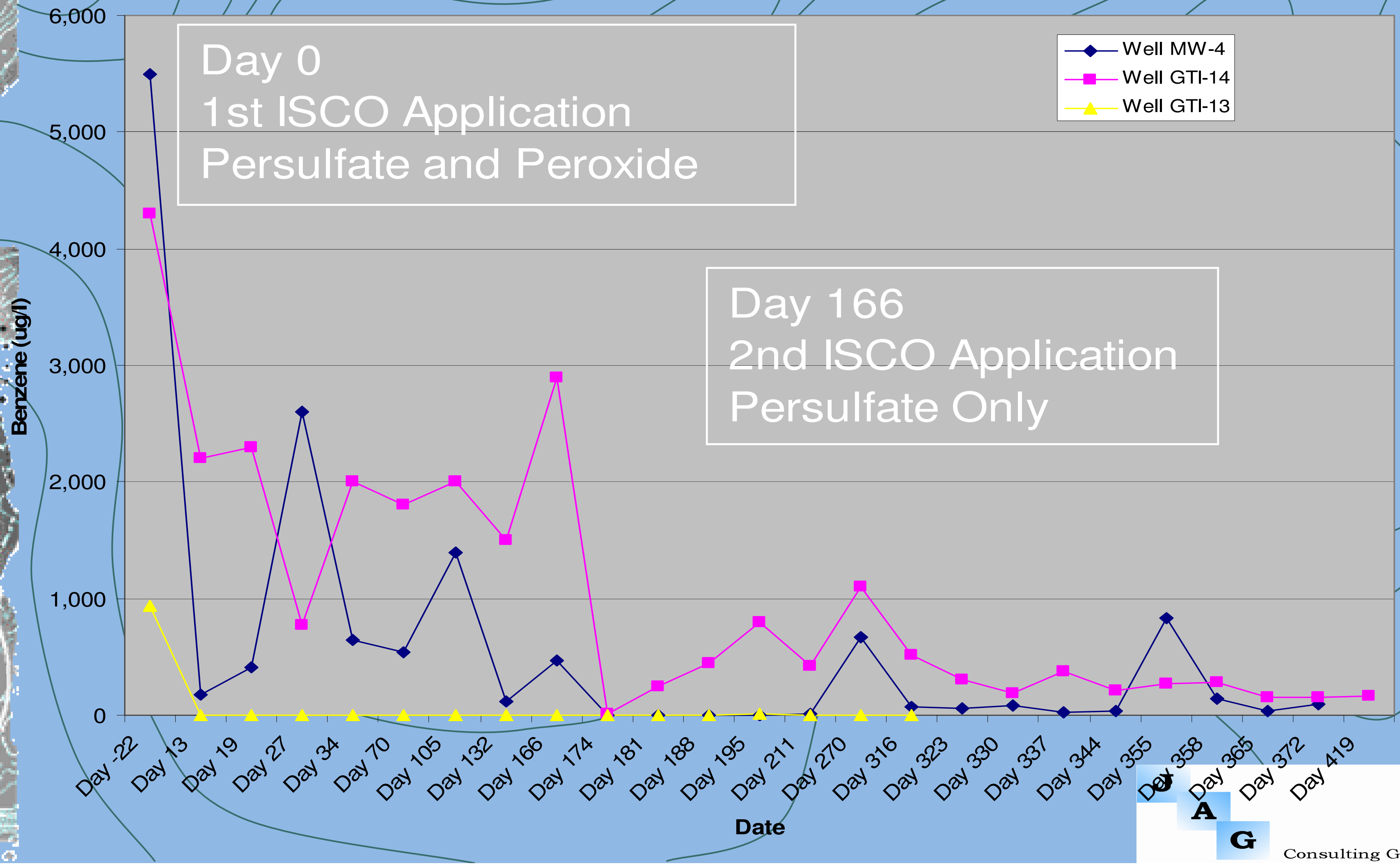
Case Study 2: Peroxide Activation
La Mirada, CA

Dissolved Benzene Reductions Following ISCO Treatment



Day 0
1st ISCO Application
Persulfate and Peroxide

Day 166
2nd ISCO Application
Persulfate Only

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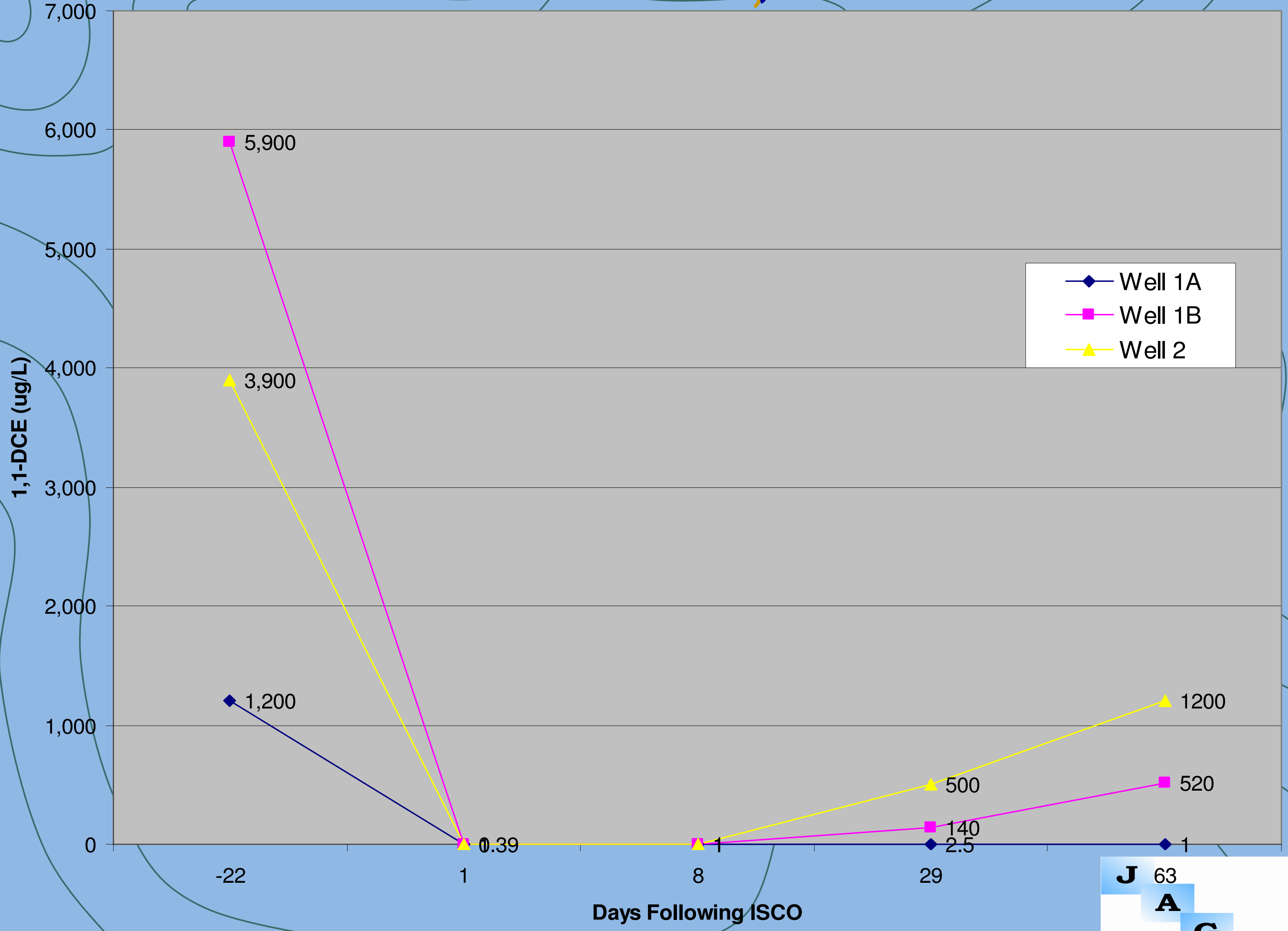
Case Study 3: High pH (Alkaline) Activation
Santa Ana, CA

- 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



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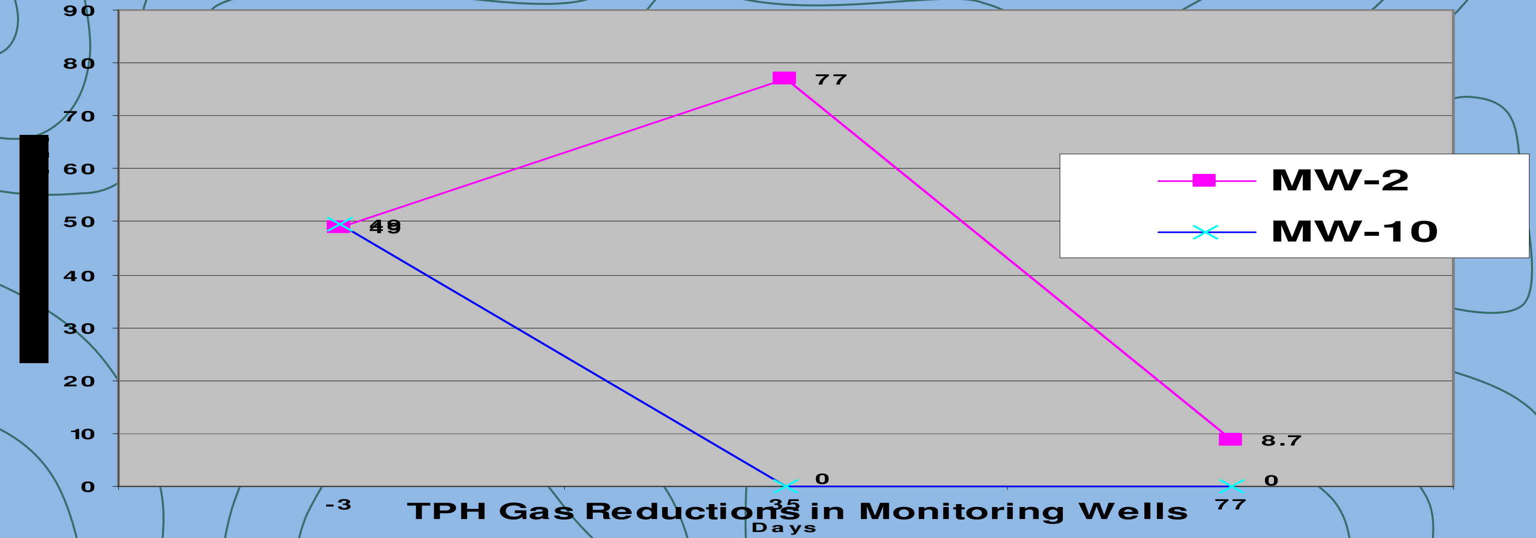
Case Study 4: High pH (Alkaline) Activation Huntington Harbor, CA

- 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

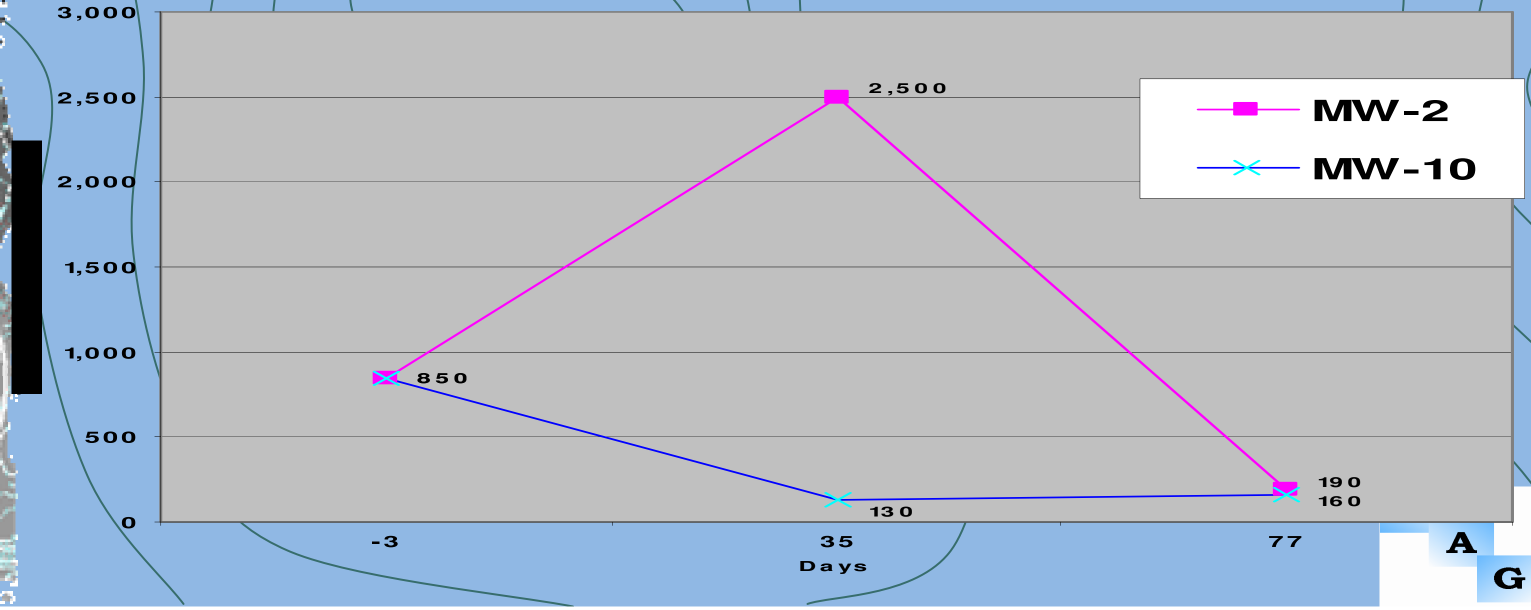
- Reduced TPH gas, BTEX, and MTBE Levels by 78% to 100%
- Project Performed by JAG Consulting and Tait Environmental

Case Study 4: High pH Activation Huntington Harbor, CA

BTEX Reductions in Monitoring Wells



TPH Gas Reductions in Monitoring Wells



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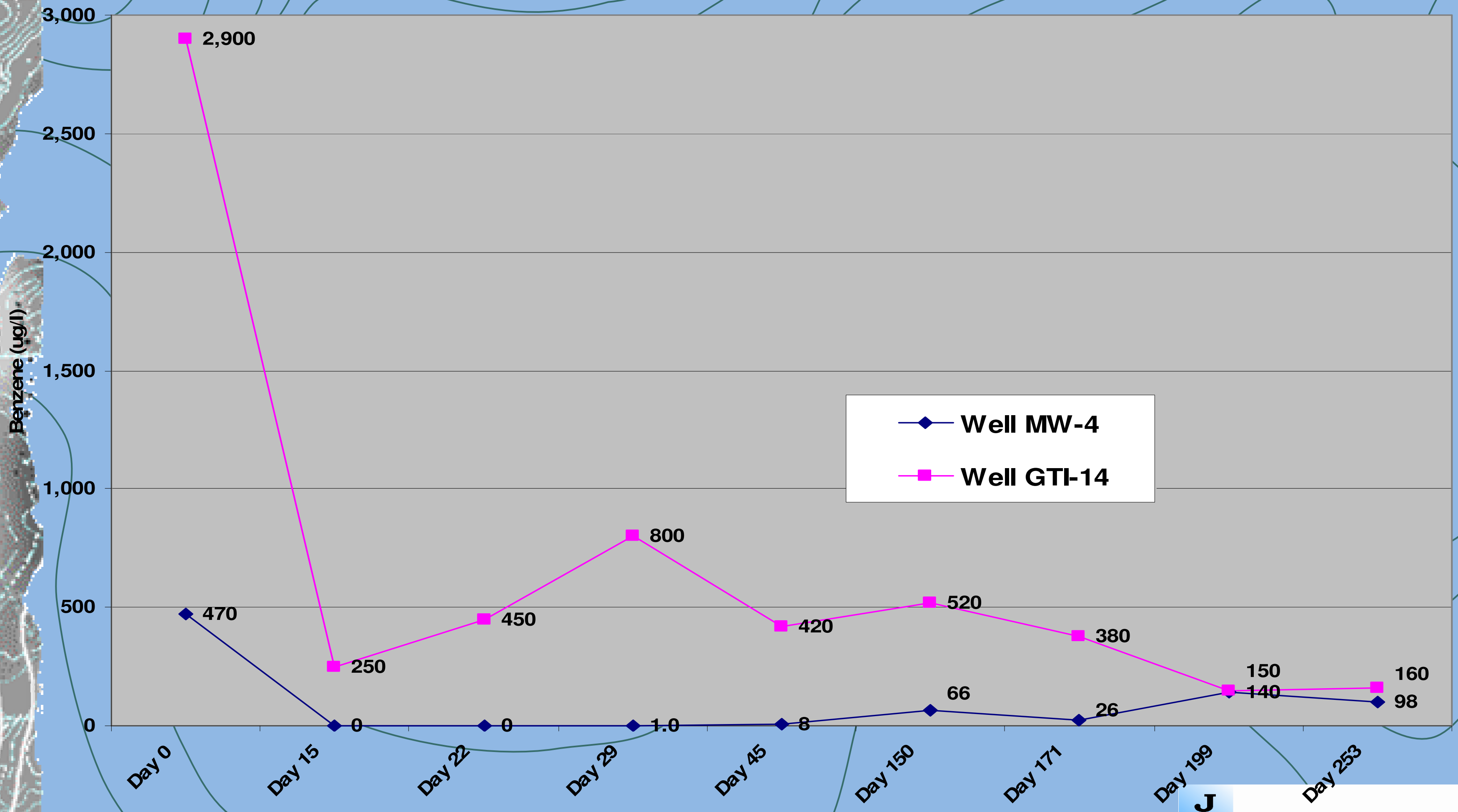
Case Study 5: Ferrous Sulfate Activation
La Mirada, CA

- 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

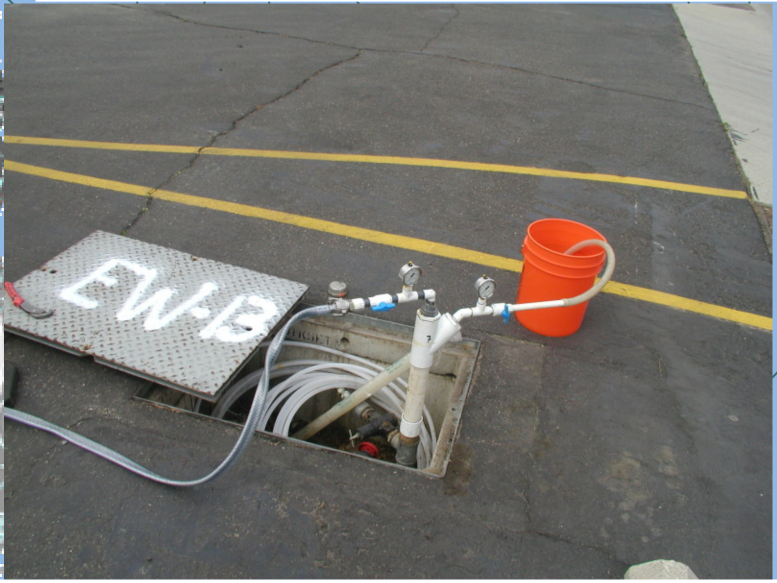
Case Study 5: Benzene Reductions Using Ferrous Sulfate Activation
La Mirada, CA



J A G Consulting Group, Inc.

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



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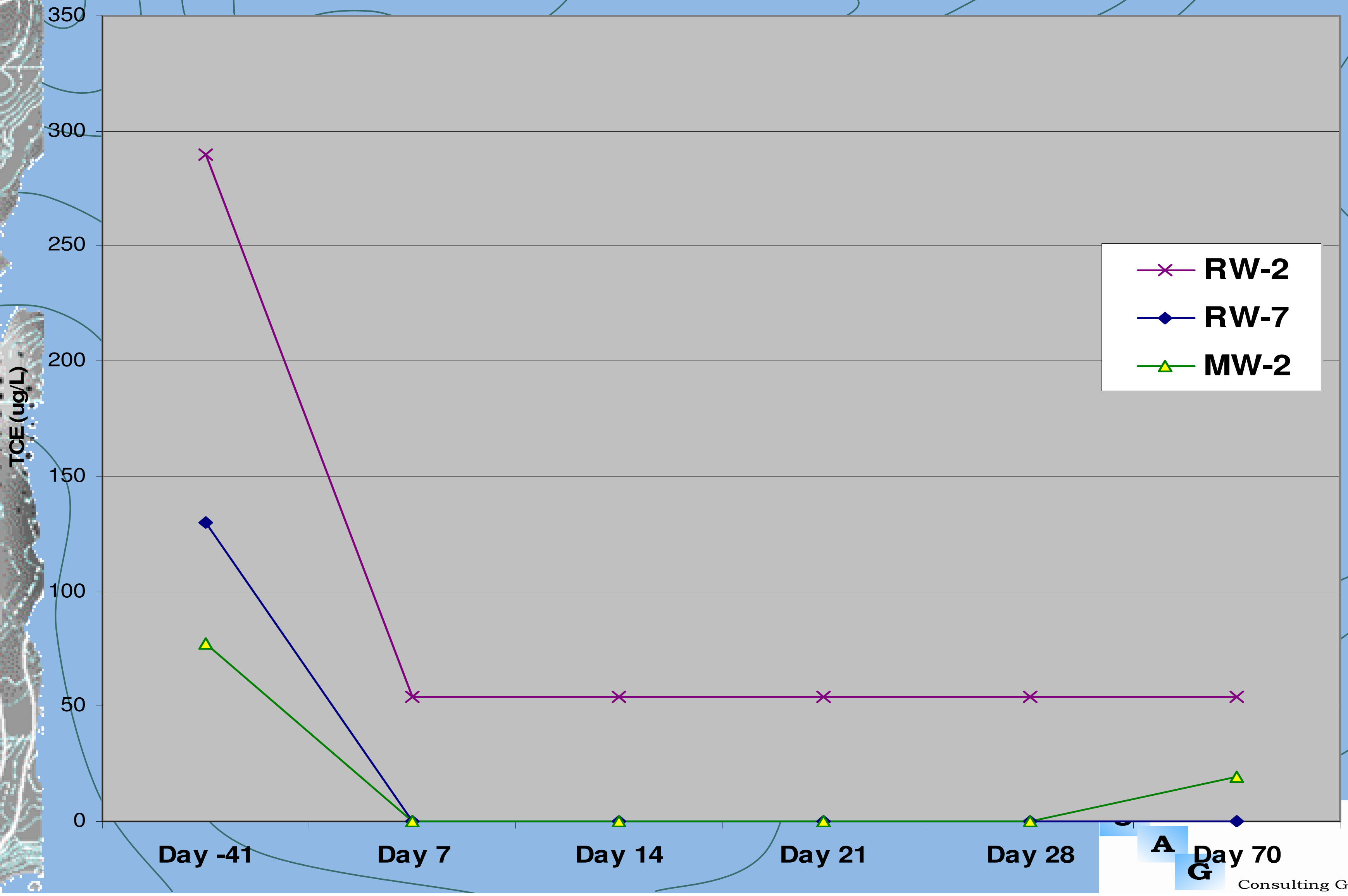
Case Study 6: TCE Reductions Using Iron EDTA



Consulting Group, Inc.

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

JAG Consulting Group, Inc.