

OPTIMIZATION OF A CHEMICAL OXIDATION TREATMENT TRAIN PROCESS FOR GROUNDWATER REMEDIATION

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ABSTRACT

A novel in-situ chemical oxidation (ISCO) optimization process has been shown to be effective for the cleanup of groundwater VOC contaminants, especially those sites with high levels of adsorbed mass. The ISCO treatment train is initiated with the catalyzation of hydrogen peroxide (Fenton's reaction) followed by the activation sodium persulfate. This combined peroxide/persulfate treatment is a newly refined treatment technology approach that utilizes both the heat and hydroxyl radicals given off by the catalyzation of hydrogen peroxide to activate the sodium persulfate.

The optimization of the ISCO treatment train process is achieved through the continuous monitoring of several Fenton's reaction parameters and then controlling the application of the hydrogen peroxide to maintain the reaction temperature within an optimal range. Continuous monitoring of temperature is performed by placing temperature probes within the annular space adjacent to the screened interval of the wells. The optimum temperature range of the Fenton's reaction has been found to be between 140 to 180 degrees Fahrenheit. At this temperature range, the catalyzed hydrogen peroxide optimally generates hydroxyl radicals and superoxide radicals without excessive decomposition of the hydrogen peroxide. The combined effect of the free radicals and elevated temperatures is very effective in desorbing contaminants from the soil particles and then mass transferring them into a dissolved phase. The Fenton's reaction is short-lived (4-10 hours) and may be expended before the dissolved phase contaminants are destroyed. However, when used with activated persulfate, the sulfate radicals continue to attack the residual dissolved mass that remains, since it is active for up to 30 days in the environment.

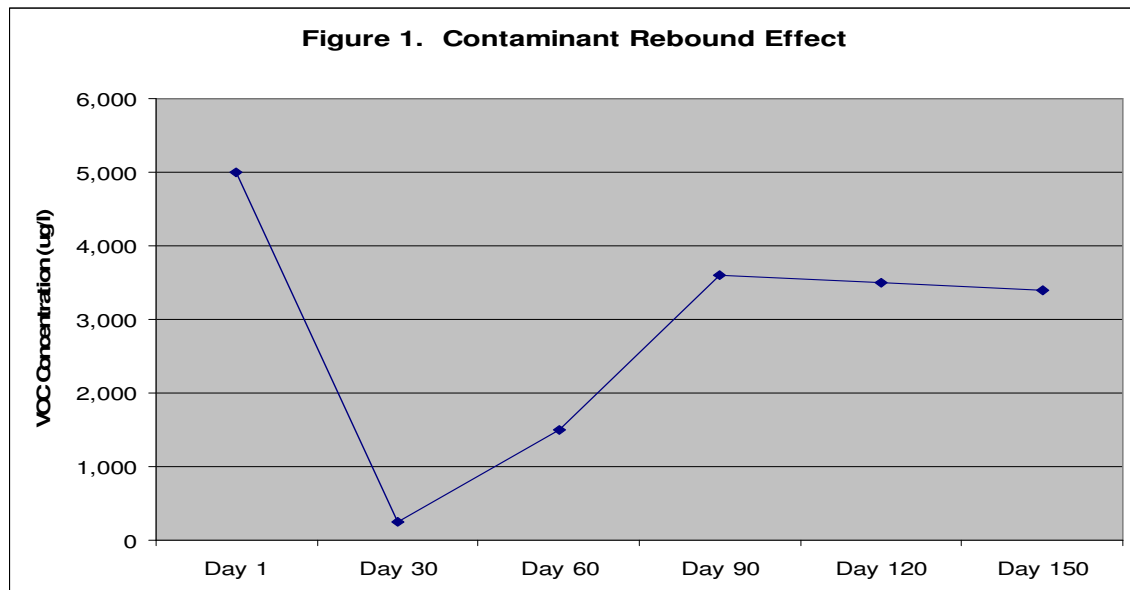
The combined application of activated persulfate and catalyzed hydrogen peroxide can eliminate the contaminant rebound effect and the repeat applications that are often required when performing conventional ISCO treatment, resulting in substantial cost savings. This ISCO treatment train technology has been successfully used on all types of petroleum hydrocarbons, chlorinated hydrocarbons, and a variety of recalcitrant compounds, such as MTBE, methylene chloride, 1,4-dioxane, PCBs, PAHs, and others.

INTRODUCTION

Marginally effective ISCO treatment of VOC contaminated sites with high adsorbed mass have been reported by numerous investigators. This is primarily due to the fact that ISCO and other in-situ remediation technologies (as well as pump and treat) are generally

limited to the treatment of dissolved phase contaminants. Contaminant rebound often occurs at these sites, since the adsorbed mass is still present after treatment and the adsorbed contaminants re-partition into the dissolved phase after several months. Based on data collected from over 50 remediation sites (Carvel 2005), the adsorbed phase mass may be as much as 3 to 10 times higher than the dissolved phase mass. High adsorbed mass is typically observed at petroleum hydrocarbon sites that have extensive smear zones and at groundwater formations comprised predominantly of silts and clays. Typically, clean sand and gravel formations have much lower percentages of adsorbed mass compared to dissolved mass.

A typical rebound effect observed at a VOC contaminated site with high adsorbed mass is shown in Figure 1. Dissolved phase contaminant levels are reduced immediately upon ISCO treatment (observed over the first 30 days) and then a contaminant rebound effect occurs after 60-90 days due to re-partitioning of the adsorbed contaminants.



ISCO TREATMENT OF DISSOLVED AND ADSORBED MASS

ISCO technologies have varying degrees of effectiveness in treatment of adsorbed mass. In general terms, potassium permanganate and sodium persulfate are ineffective in the treatment of adsorbed mass, while catalyzed hydrogen peroxide is very effective in the desorption of contaminant mass and transferring it to the dissolved phase.

Potassium permanganate (and sodium permanganate) can provide effective treatment of chlorinated ethenes (PCE, TCE, DCE, etc), but this oxidant destroys only the dissolved phase portion of the contaminant plume. Contaminant rebound is typically observed at permanganate ISCO projects and several treatment events (3 or more) are commonly implemented to attain the low cleanup levels required for site closure (low ppb range).

Activated sodium persulfate is a stronger oxidant than permanganate and can destroy a much wider range of contaminants (including several recalcitrant compounds), but this

technology also relies on attacking the dissolved phase contaminants. Contaminant rebound is also commonly observed when using persulfate on high adsorbed phase sites and multiple treatment events may be required.

Catalyzed hydrogen peroxide (a Fenton's-like reaction) differs from other ISCO technologies in that it generates excessive heat (exothermic reaction) which is effective in stripping the absorbed contaminants from the soil and converting it to a dissolved phase. The desorption of the contaminant mass becomes effective when temperatures are increased to approximately 115 to 120 degrees Fahrenheit. The Fenton's-like reaction creates hydroxyl radicals and superoxides which are highly effective oxidizing agents but have a very short life span of minutes and hours. Often times, the catalyzed peroxide is quickly expended before all the dissolved phase contaminants are contacted and destroyed.

A novel ISCO treatment train process utilizing catalyzed hydrogen peroxide combined with activated persulfate has been shown to be effective in treatment of adsorbed VOCs without the rebound effect. This newly refined technology capitalizes on the combined benefits of contaminant desorption, dissolution, and long-term destruction of dissolved phase contaminant mass, since the persulfate remains active for a longer period of time (up to 30-40 days) and will continue to attack the residual dissolved mass.

THE IMPORTANCE OF ACCURATE MASS DISTRIBUTION

The success of an ISCO project is highly dependent upon an accurate site characterization and determination of the three phases of contaminant mass distribution: dissolved, absorbed, and free phase (LNAPL or DNAPL). Without an accurate determination of the total contaminant mass and the mass distribution, ISCO projects are at risk of attaining too little treatment or are mistakenly assumed to be failures. An example would include an ISCO project designed to destroy a moderate level of dissolved mass without knowledge that high levels of absorbed contaminant mass are present. A second example would be a site where LNAPL or DNAPL is unexpectedly discovered during ISCO treatment. A third example would be a site where the contaminant of concern is thought to be restricted one constituent, but later found to have other contaminant sources. Successful contaminant reduction requires complete contaminant definition. As with any chemical engineering solution, an accurate mass balance is necessary to attain optimal results.

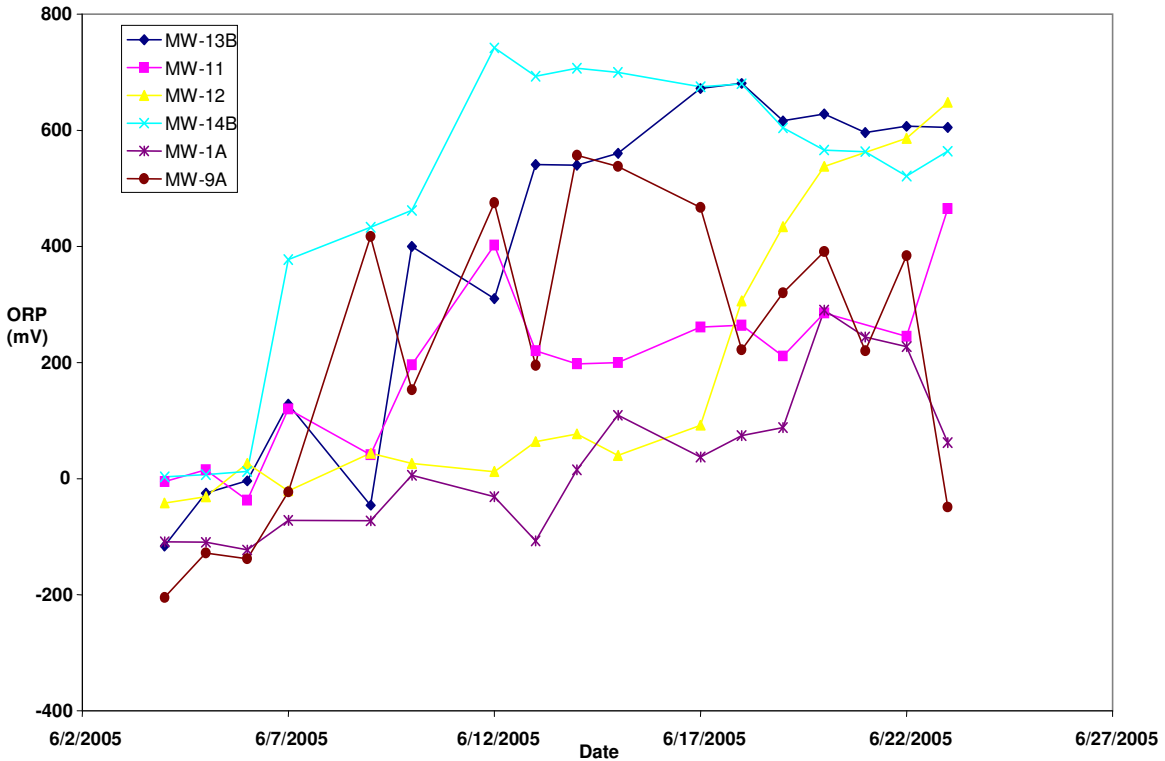
MONITORING FOR OXIDANT DISPERSION

During application of ISCO, specific field parameters are monitored to ensure that the estimated radius of treatment is attained and that an oxidizing environment is maintained within the treatment zone. Routine field measurements of pH, conductivity, dissolved oxygen, temperature, and oxidation-reduction potential (Redox or ORP) are collected in order to confirm oxidizing conditions are being maintained .

ORP is the most important field parameter for confirmation that the oxidant is adequately dispersed within the treatment zone. ORP values in the range of +200 to +600 millivolts

(mV) should be maintained during treatment. A graph illustrating the increase in ORP levels during ISCO application at a site in Los Angeles County, CA is shown in Figure 2 below.

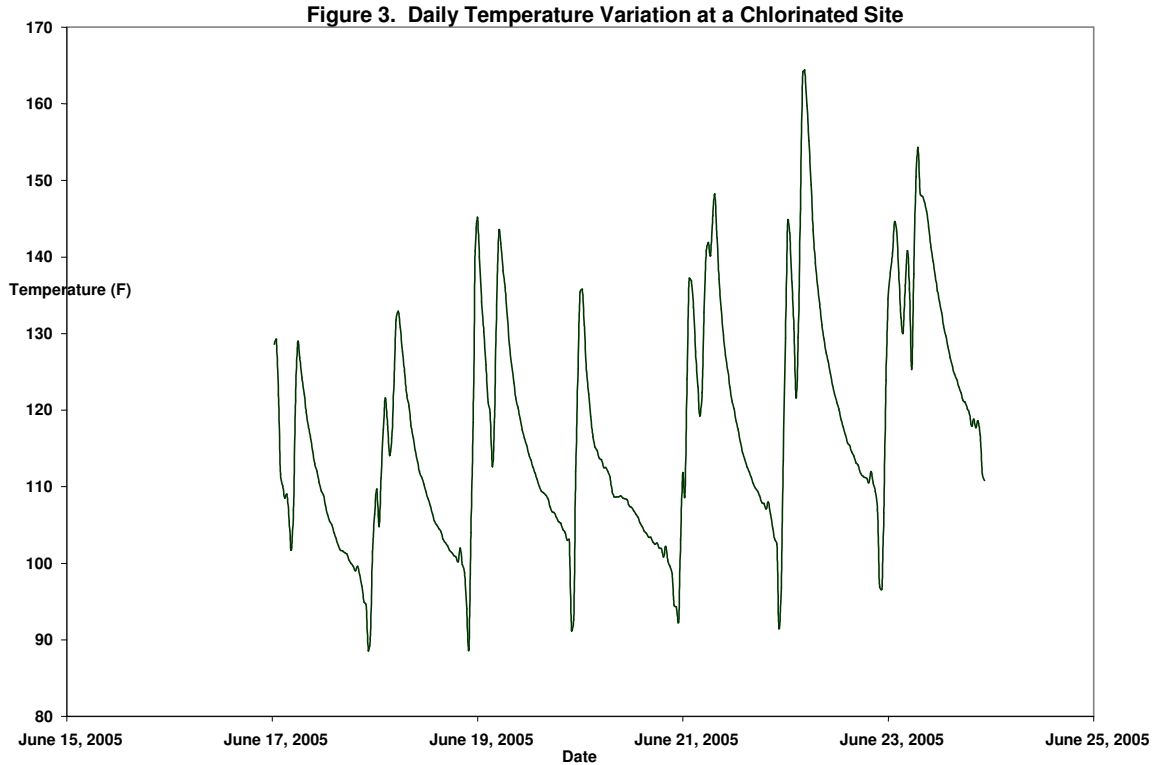
Figure 2. Flucuations in ORP During Oxidant Application



MAINTAINING OPTIMUM IN-SITU TEMPERATURES

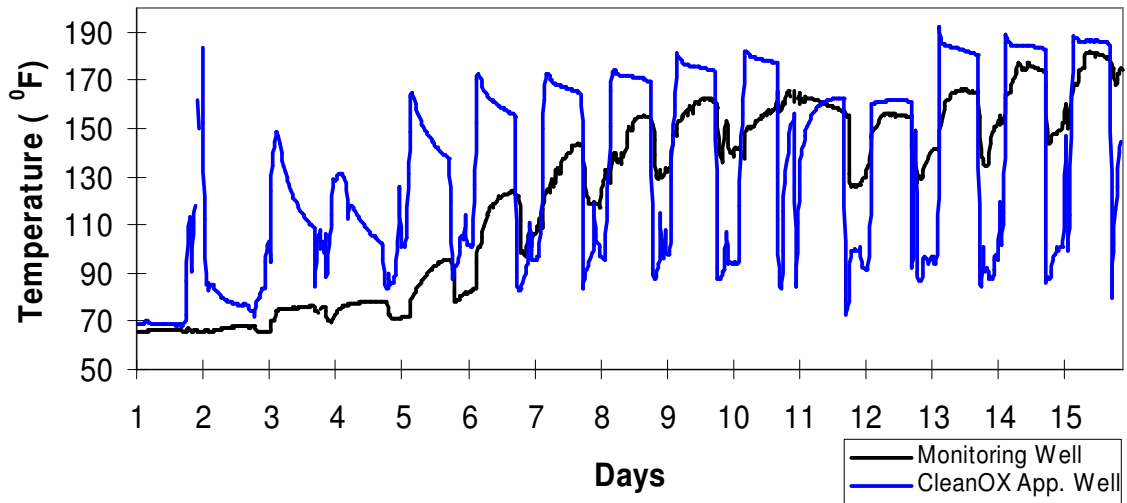
Monitoring of in-situ temperatures is performed by placement of thermocouples (temperature probes) in the application wells during installation. The thermocouples are placed within the annular space adjacent to the screened interval so that the temperature of the catalyzed peroxide reaction can be measured in-situ. The thermocouples are connected to a continuous temperature recorder where the data may be plotted for interpretation and optimization while in the field. The data are also downloaded for computer storage and reporting purposes.

For treatment of chlorinated compounds, the optimum temperature range of the catalyzed peroxide reaction has been determined to be between 120 to 160 degrees F. At these temperature ranges, the catalyzed hydrogen peroxide optimally generates hydroxyl radicals and superoxides without excessive decomposition of the hydrogen peroxide. The combined effect of hydroxyl radicals and elevated temperatures are very effective in desorbing contaminants from the soil particles and then mass transferring them into a dissolved phase. A temperature graph illustrating the temperature variation at a chlorinated site in Los Angeles County, CA is shown in Figure 3 below.



For treatment of petroleum hydrocarbons, the optimum temperature range is slightly higher, between 140 to 180 degrees F. A temperature graph illustrating the temperature variation at a petroleum hydrocarbon site is shown in Figure 4 below.

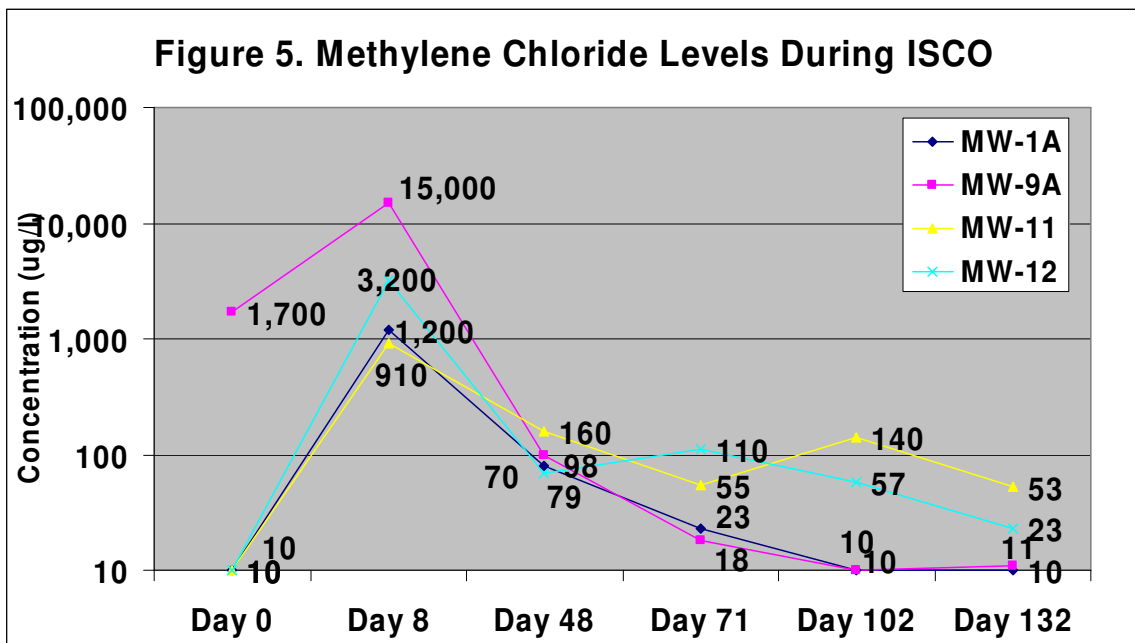
Figure 4. Temperature Variation at a Petroleum Hydrocarbon Site



The combined application of activated persulfate and catalyzed hydrogen peroxide can eliminate the contaminant rebound effect that is often observed when treating the dissolved phase contaminants only. This treatment train process can also eliminate the

repeat applications that are often required when performing Fenton’s treatment alone, resulting in substantial cost savings.

Figure 5 below illustrates the immediate conversion of adsorbed mass to dissolved mass that occurs in the first few days of an ISCO treatment using the treatment train approach. This ISCO project involved the treatment of elevated levels of methylene chloride at a site in Los Angeles County, California. In monitoring well MW-9A, the baseline concentration (Day 0) of methylene chloride was 1,700 ug/l. On Day 8 (8 days following the completion of ISCO application), the methylene chloride level was 15,000 ug/l, indicating that significant conversion of adsorbed mass had occurred resulting in an eight-fold increase in dissolved mass. Similar increases were observed in all the monitoring wells by Day 8. However, by Day 48 the contaminant levels were reduced by over 90% in all wells and the levels continued to decrease through 132 days (4 months).



The combined treatment train application of catalyzed hydrogen peroxide and activated sodium persulfate has been successfully applied at many sites across the U.S. involving the treatment of PCE, TCE, DCE, TCA, vinyl chloride, methylene chloride, 1,4-dioxane, all types of petroleum hydrocarbons (gasoline, diesel fuel, jet fuel) creosote, PAHs, BTEX, MTBE, and TBA (Aboulafia, et al, 2005). A summary of recent site reductions achieved by the ISCO treatment train process is summarized in Table 1 below.

Table 1. ISCO Treatment Train Projects Completed

Project Type	Project Location	Primary Contaminants	No. of Application Wells	Contaminant Reduction	Comment
Bulk Fuel Terminal	Southlake, Texas	Benzene and Vinyl Chloride	7 - Pilot Scale 94 - Full Scale	Pilot: 84% Full Scale: 80%	ISCO performed in tight clay at an active bulk fuel storage terminal.
Navy Installation	Virginia Beach, VA	Chlorinated Solvents (PCE, TCE)	35	97%	Highly successful full scale project.
Former Chemical Plant	Rancho Dominguez, CA	Methylene Chloride	23	94% to 97%	Performed under a building, in clayey soils with DNAPL present.
Gasoline Station	Duluth, Georgia	TPHg and BTEX	42	75%	ISCO performed in tight clay with LNAPL..
Manufacturing Facility	St. Mary's, Pennsylvania	Chlorinated Solvents (PCE, TCE)	12	83%	Also reduced soil concentrations by 93%.
Pipeline Rupture	Kentwood, LA	TPHg and BTEX	22	Removed 2.5 ft apparent thickness LNAPL Product	Clayey sand. Application performed within 10 feet of four active pipelines.
Gas Station Site	New Castle, IN	TPHg and BTEX	8	94-99%	Free phase LNAPL removed from one monitoring well

REFERENCES

1) Aboulafia, Isaac, Larry D. Rader, R. Thomas Numbers and Richard T. Cartwright, 2005. *Real-Time Effective Performance Monitoring of In-Situ Chemical Oxidation Projects*. Presented at the ORTs-4 Conference, Chicago, IL October 2005.

2) Carvel, Douglas D., 2005. *Innovative Activated Sodium Persulfate and Peroxide NAPL Remediation at Low Permeability Sites*. Presented at the ECOR Conference, 2005.

3) Interstate Technology & Regulatory Council (ITRC), 2005. In-Situ Chemical Oxidation Team. *Technical and Regulatory Guidance for In Situ Chemical Oxidation of Contaminated Soil and Groundwater (Second Edition)*; ITRC, January 2005.