WORK PLAN TO PERFORM A POTASSIUM PERMANGANATE PILOT STUDY

HANGAR D, WESTCHESTER COUNTY AIRPORT

WHITE PLAINS, NEW YORK

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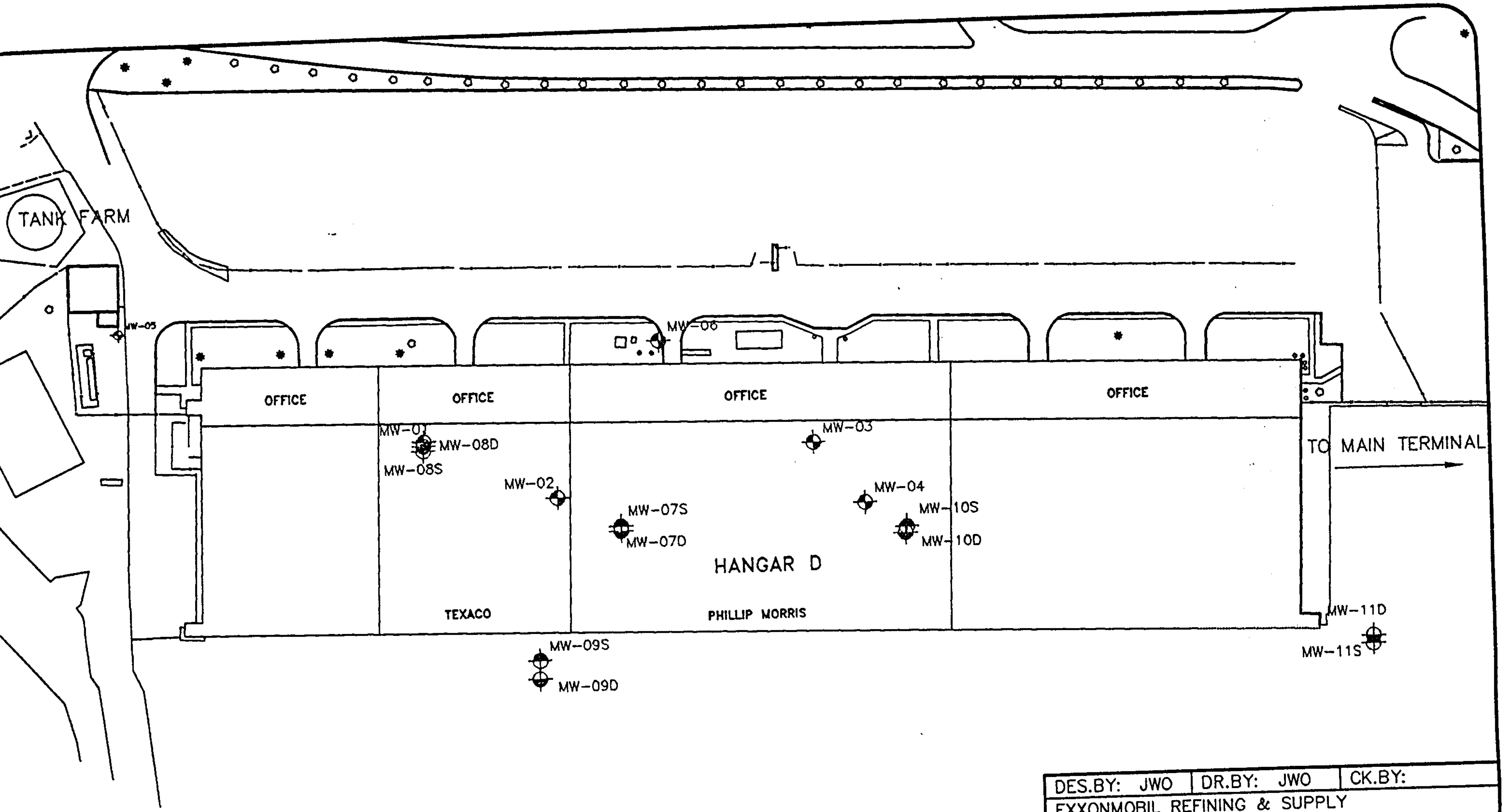
1. INTRODUCTION AND PILOT TEST OBJECTIVES

Woodard & Curran proposes to perform a Potassium Permanganate ($KMnO_4$) Addition Pilot Study at the Westchester Country Airport located in White Plains, New York. The pilot test will be conducted in the area of existing monitoring wells MW-01, MW-02, MW-08S and MW-08D located in the Hanger D. Potassium permanganate will be injected into the subsurface using temporary injection points (drive points) installed through the hangar floor. A Site Plan is attached as Figure 1.

The objectives of the Pilot Test are to: 1) document the feasibility of utilizing potassium permanganate to reduce the contaminant mass in the source area groundwater at the Site; and 2) provide site specific information that can be used to optimize future potassium permanganate activities and cost to closure estimates for the Site.

1.1 BASIS FOR IN-SITU CHEMICAL OXIDATION USING $KMnO_4$

Potassium permanganate is a common oxidant widely used in the water treatment industry to remove dissolved metals and in the sewage treatment industry to treat sulfide odors. $KMnO_4$ will react with and oxidize a wide range of common organic compounds, relatively quickly and completely. In particular, $KMnO_4$ reacts rapidly with the non-conjugated (i.e. non-aromatic) double bonds in chlorinated ethenes such as trichloroethylene (TCE), tetrachlorothylene (PCE), dichloroethylene (DCE) isomers, and vinyl chloride. Permanganate is generally less reactive with chlorinated ethanes such as dichloroethane (DCA) and trichloroethane (TCA). However, W&C's experience with this technology, as well as others (refer to p. 107, Clayton, W.S., et al, "A Multisite Field performance Evaluation of In-Situ Chemical Oxidation using Permanganate" attached), has shown good reductions in these compounds under certain site conditions. In general, the effectiveness of permanganate to reduce TCA and DCA depends on the concentrations of competing reduced/oxidizable species present at the Site. These include chlorinated ethenes, other contaminants, organic carbon sources, and inorganic compounds such as iron and manganese. The monitoring well network currently in place at the Site has delineated the extent of both the ethane and ethane plume. The plume is currently limited to the area beneath the Texaco Hangar and the adjacent Phillip Morris Hangar and not potential receptors to the groundwater contamination has been identified within or in the vicinity of the plume.



NOTES

1. ALL LOCATIONS & DIMENSIONS OF SITE FEATURES, PROPERTY LINES & SAMPLING LOCATIONS ARE APPROX.
2. BASE MAP PROVIDED ELECTRONICALLY FROM XDD, INC. IN FEBRUARY 2001.

LEGEND

MW-01 ⊕ - OVERBURDEN MONITORING WELL
MW-08S ⊕ - SHALLOW BEDROCK MONITORING WELL
MW-08D ⊕ - DEEP BEDROCK MONITORING WELL

DES.BY: JWO	DR.BY: JWO	CK.BY:

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WESTCHESTER COUNTY AIRPORT
PILOT STUDY

FIGURE 1
HANGAR D SITE MAP

SCALE: 1" = 100'	JOB NO.: 205265
DATE: MARCH 2001	SHEET: PS FIG 1

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W&C will perform the pilot test activities to gauge the effectiveness of this technology to address both chlorinated ethenes and ethanes present at the Site. The data generated during the pilot test will be evaluated against the project objectives, specifically the ability of the permanganate to reduce the contaminant mass of all the compounds of concern present at the Site, including TCA and DCA which are both present at the site at concentrations above the New York Groundwater Standards. The results of the pilot test will be presented and discussed in the Feasibility Study to be completed at the Site. As required, the Feasibility Study will present the most appropriate and comprehensive remedial approach to address all of the compounds of concern at the Site.

Permanganate oxidizes the chlorinated ethenes to CO2, water and carbonate ions. The balanced chemical equations for permanganate oxidation of TCE, PCE and VC are:

PCE: $4KMnO_4 + 3C_2Cl_4 + 4\ H_2O \rightarrow 6CO_2 + 4MnO_2 + 4K^+ + 12Cl^- + 8H^+$

TCE: $2KMnO_4 + C_2HCl_3 \rightarrow 2CO_2 + 2MnO_2 + 2K^+ + 3Cl^- + H^+$

VC: $10KMnO_4 + 3C_2H_3Cl \rightarrow 6CO_2 + 10MnO_2 + 10K^+ + 3Cl^- + 7OH^+ + H_20$

Potassium Permanganate is applied as a solution. The solution is relative stable and generally consumed only through reaction with the contaminants or other reduced species. W&C experience has shown that a 2 -5 % solution of $KMnO_4$ works best for field applications.

In situ oxidation is a chemical reaction. The effectiveness of treatment depends on three factors: 1) the kinetics of the reaction between the permanganate and the contaminant; 2) the contact between the oxidant and the contaminants; and 3) competitive reactions of permanganate with other reduced/oxidizable species in the aquifer. W&C's experience has shown that significant oxidation can be observed in as little as a few hours after addition, but travel times for permanganate to migrate away from the addition point may be on the order of days to weeks depending on the rate of groundwater flow. The pilot test activities proposed by W&C will provide the information required to evaluate the feasibility and total expected costs of utilizing in-situ $KMnO_4$ applications to meet the project objectives.

Additional information regarding in-situ chemical oxidation using $KMnO_4$ and W&C's experience with this technology is in Attachment 1 and 2.

2. TEST ACTIVITIES

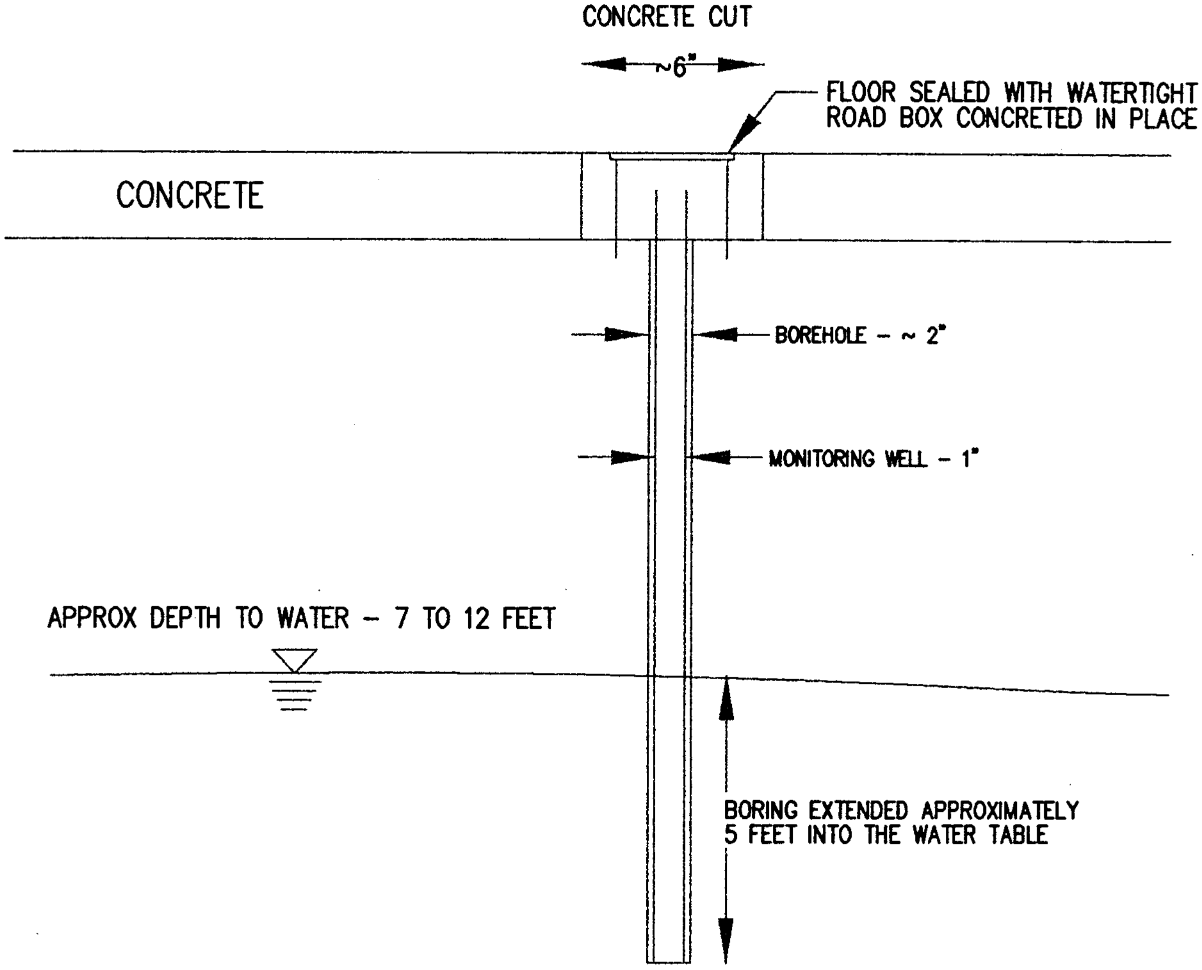
Woodard & Curran will perform the following activities as part of the $KMnO_4$ Pilot Study at the Westchester County Airport Hangar D site.

Pre-Addition	Addition Activities	Post-Addition
1. Prepare a Project Specific Health and Safety Plan. 2. Perform additional assessment activities to better define the vertical and horizontal extent of the source area. 3. Complete five test monitoring wells to better document the results of the $KMnO_4$ addition. 4. Perform pre-addition groundwater monitoring and sampling activities.	5. Prepare $KMnO_4$ slurry solution for injection into subsurface via Geoprobe borings. 6. Addition of 50-100 lbs. of $KMnO_4$ at each of the borings located at varying locations and depths across the source area.	7. Perform post-addition field monitoring of groundwater quality parameters. 8. Collect groundwater samples from test monitoring wells for analysis one month and three months after addition activities. 9. Include a summary of findings and evaluation of the pilot test results in the Feasibility Study being developed for the Site.

2.1 PRE-ADDITION ACTIVITIES

W&C proposes to perform the following pre-test activities:

- Prepare a Project Specific Health and Safety Plan;
- Perform additional assessment activities within the source area; which will include:
  - Collect and analyze for VOCs in soil and groundwater samples from five (5) soil borings using a Geoprobe sampling device in the MW-01 and MW-02 areas to better delineate the location and extent of the source area soil and groundwater contamination. Detail A presents the design details for the geoprobe soil borings and monitoring wells;
  - Complete five (5) of the soil borings into temporary monitoring wells for use during the pilot study;



NOTE:

THE 2 INCH BORING IS ADVANCED USING A VIBRATORY DRILL RIG MOUNTED TO EITHER AN ALL TERRAIN VEHICLE OR A PICK-UP TRUCK. A FOUR FOOT SOIL SAMPLE IS VIBRATED INTO THE GROUND TO COLLECT SOIL SAMPLES AND TO ADVANCE THE BOREHOLE. ONCE THE DESIRED DEPTH HAS BEEN REACHED, A 1 INCH PVC MONITORING WELL IS INSTALLED IN THE BOREHOLE AND FITTED WITH A WATERTIGHT ROADBOX WHICH IS CONCRETED INTO PLACE. IF NOT MONITORING WELL IS TO BE INSTALLED, THE BORING WILL BE STILL BE COMPLETED WITH A ROADBOX TO ALLOW EASY ACCESS THROUGH THE SLAB IN THE FUTURE.

DES.BY: JWO	DR.BY: JWO	CK.BY: MED

WESTCHESTER COUNTY AIRPORT
POTASSIUM PERMANGANATE PILOT STUDY
DETAIL A
GEOPROBE SUBSURFACE INVESTIGATION DETAILS

SCALE: NONE	PROJECT NO: 205265
DATE: JUNE 2001	DETAILA

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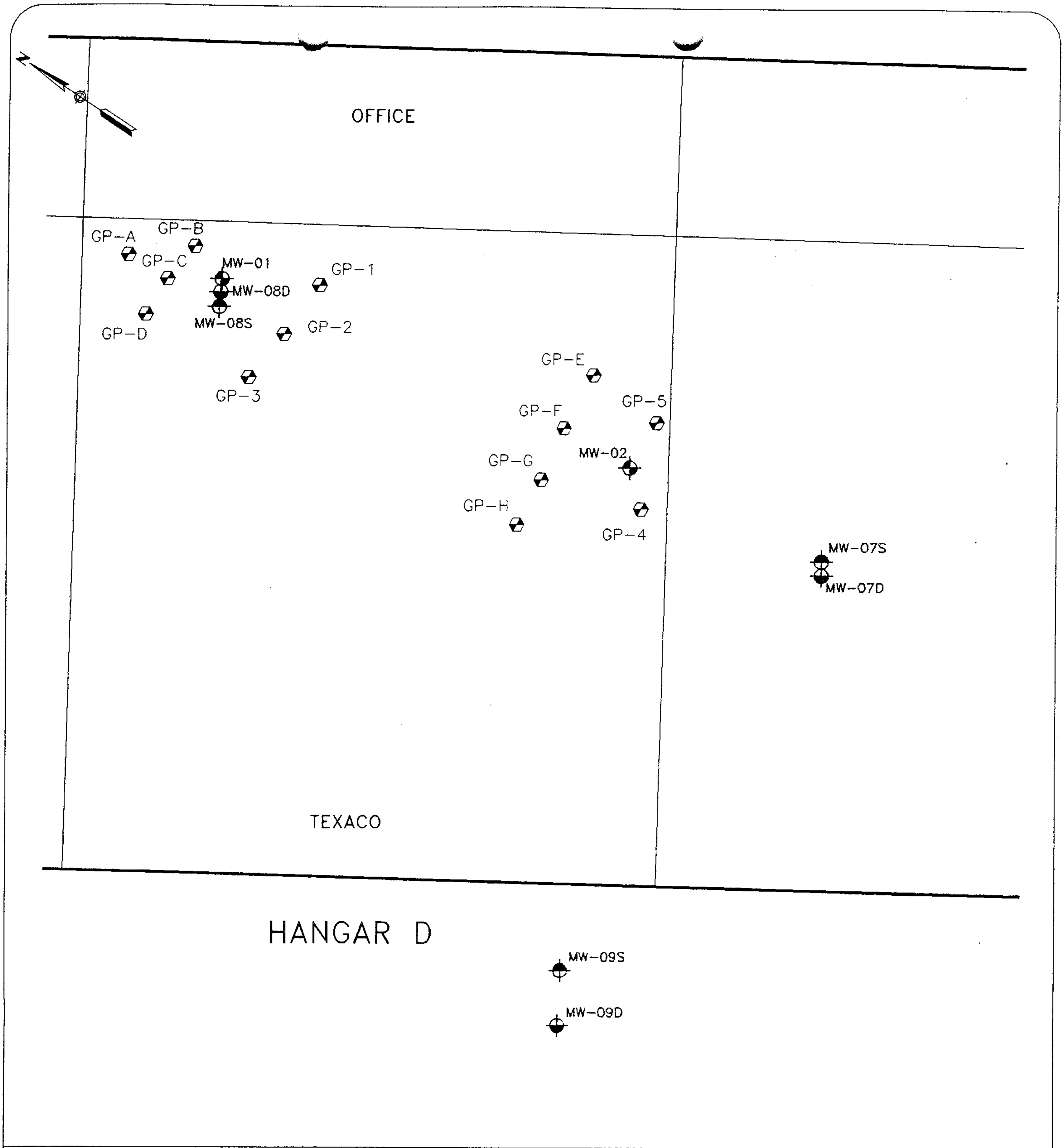
- Perform "Base Line" groundwater sampling and monitoring activities which will include:
    - Collection and laboratory analysis of groundwater samples from 10 (new and pre-existing) monitoring wells for VOCs by EPA Method 8260 and the presence of manganese and chloride ion.
    - Monitor field groundwater quality parameters (dissolved oxygen, Oxidation-reduction potential, pH, temperature, conductivity) from 15 monitoring wells prior to performing $KMnO_4$ addition activities.

Based on the current understanding of the site, W&C proposes to perform the $KMnO_4$ addition test activities in the area between MW-01 and MW-02, as shown on Figure 2. Table 1 below lists the existing Site wells and the proposed new wells for use during the pilot test.

TABLE 1: PROPOSED TEST MONITORING WELLS

Well ID	**Pilot Test Function**
Existing Monitoring Wells to be used during Pilot Test Activities	
MW-01	Source area test monitoring well
MW-08S	Source area test monitoring well
MW-08D	Source area test monitoring well
MW-02	Source area test monitoring well
MW-07S	Down-gradient test monitoring well
MW-07D	Down-gradient test monitoring well
MW-09S	Down-gradient test monitoring well
MW-09D	Down-gradient test monitoring well
MW-10S	Down-gradient test monitoring well
MW-10D	Down-gradient test monitoring well
New Monitoring Wells to be used during Pilot Test Activities	
GP-1	Source area test monitoring well
GP-2	Source area test monitoring well
GP-3	Source area test monitoring well
GP-4	Source area test monitoring well
GP-5	Source area test monitoring well



LEGEND

GP-A - PROPOSED PERMANGANATE INJECTION POINT

GP-1 - PROPOSED PERMANGANATE TEST MONITORING WELL

MW-01 - OVERBURDEN MONITORING WELL

MW-08S - SHALLOW BEDROCK MONITORING WELL

MW-08D - DEEP BEDROCK MONITORING WELL

DES.BY: MED DR.BY: JWO CK.BY: MED

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POTASSIUM PERMANGANATE PILOT STUDY

FIGURE 2
PROPOSED EXPLORATIONS AND
PILOT STUDY TEST LAYOUT PLAN

SCALE: 1"=30' PROJECT NO: 205265
DATE: MARCH 2001 PILOTSTUDYFIG1.DWG

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2.2 $KMnO_4$ ADDITION ACTIVITIES

W&C proposes to inject $KMnO_4$ into the subsurface using temporary injection points (drive points) installed through the hangar floor. The potassium permanganate will be premixed in a mix tank and applied to the subsurface via eight (8) temporary injection points utilizing a Geoprobe rig and a high-pressure grout pump.

W&C proposes to inject 50 to 100 lbs. of $KMnO_4$ at eight (8) temporary injection locations (for a total $KMnO_4$ mass of approximately 400 to 800 lbs.) into the source area soils and groundwater during the injection activities. W&C bases this estimate on our past experience with $KMnO_4$ addition, current industry practice; and understanding of the Site geology, groundwater quality and contaminant mass. W&C is confident that this mass range will result in the successful completion of the injection activities, in a safe controlled manner, while also providing sufficient data related to the reduction of the contaminant mass within the test area.

The mix tank will consist of a 55-gallon open topped drum. The powdered $KMnO_4$ will be mixed with water in the 55-gallon drum, which will be placed in a secondary containment tub to minimize the chance of spills. The solution will be pumped from the mix tank to the geoprobe rig where the high pressure grout pump will be used to inject it into the aquifer.

The addition activities will be completed within the Texaco Hangar and will not impact airport activities. The two injection locations are along the walls of the hangar and therefore, addition activities should not impact work in the Texaco Hangar. The addition activities are scheduled for completion over several days. At the end of each day, the mix tank, grout pump, rig and all ancillary equipment will be cleaned an stored either in an area of the hangar where it will not be in the way, or it will be brought off site. No mixed solution will be stored overnight and dry $KMnO_4$ will not be left in the hangar overnight.

2.3 POST ADDITION ACTIVITIES

W&C proposes to perform the following post-test activities.

- Monitor field groundwater quality parameters in all test monitoring wells as follows:
    - Once per week for the remainder of the month after the addition activities;
    - Once per month for the following two months.
- Perform sampling and analysis of groundwater from 15 monitoring wells, within one month after addition activities.
- Perform sampling and analysis of groundwater from up to 15 monitoring wells, within 3 months after addition activities.

Groundwater samples will be analyzed for VOCs by EPA Method 8260 and manganese and chloride ion.

As stated in NYSDEC correspondence dated May 30, 2001, manganese will be monitoring to ensure that it does not exceed 300 ppb outside of treatment area.

2.4 SCHEDULE

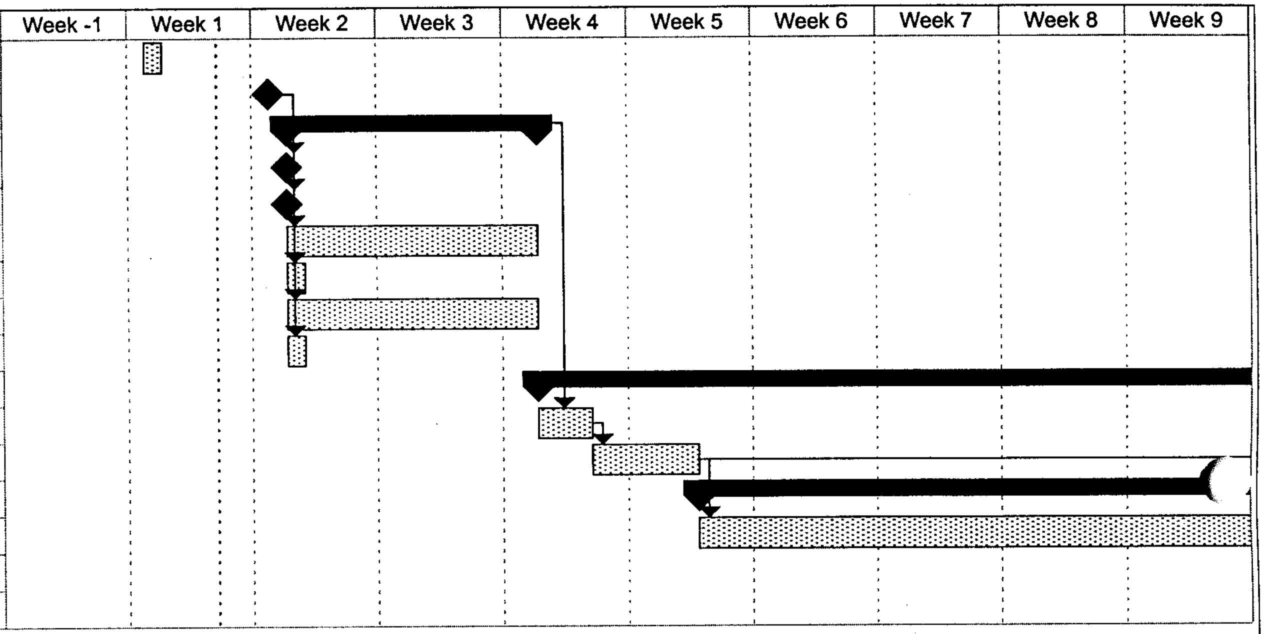
The Health and Safety Plan will be submitted to the NYSDEC for review within a week of submission of this Pilot Study Work Plan. The schedule for completion of the Pilot Study is dependent upon the schedule for the drillers upon receiving approval to proceed. Once we have received approval, we should be able to get the drillers schedule within three weeks. The schedule will also need to be approved by Texaco to minimize disruption to there operations during addition activities. A project schedule based on Weeks and not actual dates is attached to this work plan.

3. GENERATE OF REPORT OF FINDINGS

Upon completion of the pilot study activities, Woodard & Curran will incorporate the results of the pilot test activities into the Feasibility Study being developed for the Site. In addition, a short letter summarizing the results of the pilot study including the data collected will be completed and submitted to NYSDEC. The information that will be evaluated and presented in the feasibility study will include:

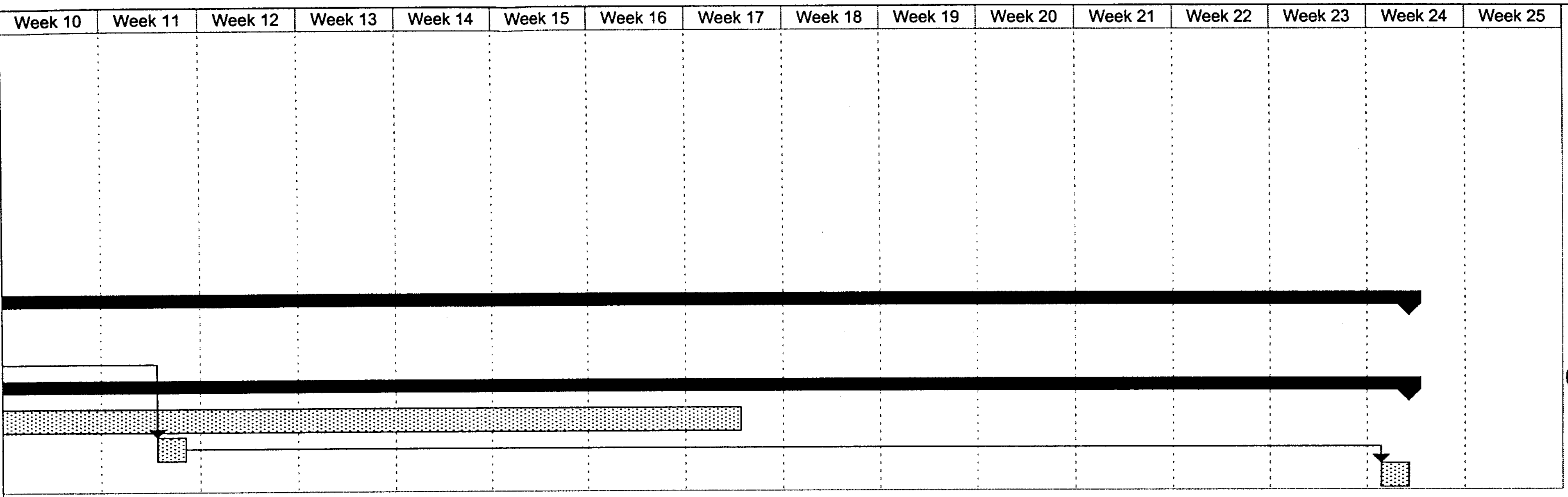
- Estimates of the mass of contaminants present in the source zone soils and groundwater;
- Contaminant percent reductions observed as a result of pilot test activities;
- Evaluation of the flow and persistence of $KMnO_4$ in the subsurface; and
- A basis for future applications of $KMnO_4$ at the Site, including the mass of $KMnO_4$ required, the number of applications necessary and the total cost to closure estimates using $KMnO_4$ technology.

ID	❶	Task Name	Duration
1	▦	Submit Health and Safety Plan to NYSDEC	1 day
2	▦	Receive Approval from NYSDEC	1 day
3		**Mobilize Field Effort**	**10 days**
4		Notify WCA Airport	1 day
5		Notify Texaco	1 day
6		Obtain KMnO4	10 days
7	▦	Schedule Drillers	1 day
8		Schedule/Obtain Access from Texaco	10 days
9		Schedule Field Staff	1 day
10		**Field Work**	**101 days**
11		Pre-Addition Activities	3 days
12		Addition Activities	4 days
13		**Post-Addition Activities**	**94 days**
14		Monitoring Field Parameters	60 days
15		1 month groundwater sampling	2 days
16		3 month groundwater sampling	2 days



Project: Project1
Date: Fri 6/29/01

Task	▨	Rolled Up Task	▨	External Tasks	▨
Progress	▬	Rolled Up Milestone	◇	Project Summary	▬
Milestone	◆	Rolled Up Progress	▬	Group By Summary	▬
Summary	▬	Split	....		



Project: Project1
Date: Fri 6/29/01

Task	▨	Rolled Up Task	▨	External Tasks	▨
Progress	▬	Rolled Up Milestone	◇	Project Summary	▬
Milestone	◆	Rolled Up Progress	▬	Group By Summary	▬
Summary	▬	Split	⋯		

Chemical Oxidation and Reactive Barriers:

Remediation of Chlorinated and Recalcitrant Compounds

Editors: Godage B. Wickramanayake, Arun R. Gavaskar,
and Abraham S.C. Chen

A MULTISITE FIELD PERFORMANCE EVALUATION OF *IN-SITU* CHEMICAL OXIDATION USING PERMANGANATE

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Bruce K. Marvin, (IT Corporation, Concord, California)
Timothy Pac (IT Corporation, Norwood, MA)
Ernest Mott-Smith, P.E, (IT Corporation, Tampa, Florida)

ABSTRACT: Field data are presented from multiple in-situ chemical oxidation projects where potassium permanganate ($KMnO_4$) or sodium permanganate ($NaMnO_4$) were used for the treatment of chlorinated ethenes and other recalcitrant organic contaminants. The large body of field data is used to illustrate and evaluate the primary performance characteristics of the technology, including (1) subsurface permanganate transport, (2) permanganate-contaminant reaction kinetics, (3) matrix interactions and other secondary geochemical effects, (4) overall permanganate consumption, and (5) contaminants treated and overall reductions achieved. Analytical modeling and field data show that oxidant demand and permanganate reaction kinetics both exert critical control over permanganate transport. Relevant matrix interactions during in-situ oxidation with permanganate can include permanganate consumption by oxidation of native materials (such as sulfides, natural organic matter, and reduced metals) and oxidation of native materials that are more mobile in an oxidized valence state. These metals tend to quickly attenuate, by sorption and natural chemical reduction. Geochemical data show that chemical oxidation using permanganate is a highly dynamic geochemical process. Dissolved Mn is ephemeral, and primarily correlates to the presence of MnO_4^-, which is consumed by the oxidation reactions.

INTRODUCTION

Background. In-situ chemical oxidation is an emerging technology for treatment of organic contaminants. It is attractive, because it destroys contaminants in-situ, generating relatively innocuous products. In-situ chemical oxidation does not require groundwater pumping, and therefore does not generate any waste stream requiring treatment or disposal. In-situ oxidation projects can commonly be completed in a period of several months, which can reduce overall remediation costs. Furthermore, in-situ oxidation can be extremely effective for hard to treat contaminants. Treatment results can be obtained that may have been previously considered technically impractical. There are three primary issues involved in managing in-situ oxidation: (1) determining that a selected oxidant will treat the target contaminants, (2) determining the oxidant mass required for treatment, and to overcome competing oxidant demand, such as by natural organic matter, and (3) providing adequate subsurface transport of the oxidant, so that all target contaminated areas are treated

There are three primary oxidants being used for in-situ oxidation, ıcluding (in decreasing order of oxidant strength): hydroxyl radical (*OH), zone (O_3), hydrogen peroxide (H_2O_2), and permanganate ion (MnO_4^-). The rimary considerations in selecting one oxidant versus another relate to trade-offs etween oxidant strength and oxidant stability. Stronger oxidants are more ggressive and can treat more recalcitrant contaminants, but they are less stable, ıore short-lived, and more difficult to deliver in the subsurface.

This paper describes the field performance characteristics of in-situ hemical oxidation using permanganate. In light of the above background, the eader should recognize that permanganate has less oxidant strength than *OH,)$_3$, or H_2O_2, but is more persistent in the subsurface. Among the contaminants eadily oxidized by permanganate are chlorinated ethenes. The reaction of MnO$_4$ with tricholoroethene (TCE) follows: $2KMnO_4 + C_2HCl_3 \rightarrow 2CO_2 +$ $MnO_2 + 2K^+ + 3Cl^- + H^+$.

The TCE oxidation products represented above are the reaction end points, ıd in reality the contaminant oxidation proceeds by a number of intermediate eps. Yan et al. (1998) showed that the intermediate compounds for TCE xidation using permanganate were primarily cyclic esters (i.e. $MnO_4C_2HCl_3$) llowed by $HMnO_3$ and carboxylic acids ($H_aC_bO_cOH_d$).

Scope and Objectives. Since in-situ oxidation is relatively new, many of e fundamental field performance characteristics are still being learned. The proach adopted in this paper was to identify the most relevant performance iteria for in-situ oxidation using permanganate, review the relevant basic theory each, and use data from multiple field sites to determine a range of observed rformance. The primary performance criteria identified include (1) subsurface rmanganate transport, (2) permanganate-contaminant reaction kinetics, (3) atrix interactions and other secondary geochemical effects, (4) overall rmanganate consumption, and (5) overall contaminant reductions achieved.

JBSURFACE PERMANGANATE TRANSPORT

fective subsurface permanganate transport is required to deliver the oxidant to ntaminants in the subsurface. In-situ oxidation is dependent on oxidant nsport, not contaminant transport. Clayton (1988) indicated that second order idant reactions with contaminants provide a limit on oxidant transport. Since rmanganate reaction rates are faster in the presence of oxidizeable materials, we ı expect more limited permanganate transport in areas of a site with higher ntaminant concentrations. As treatment proceeds, and the mass of oxidizeable aterial is reduced, permanganate transport will be greater.

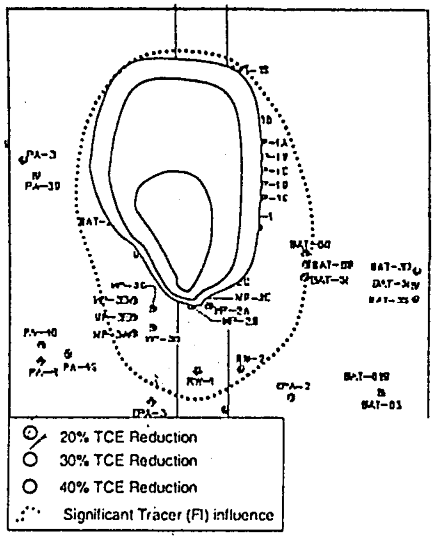


Figure 1. Results of Combined Tracer-Permanganate Injection Test.

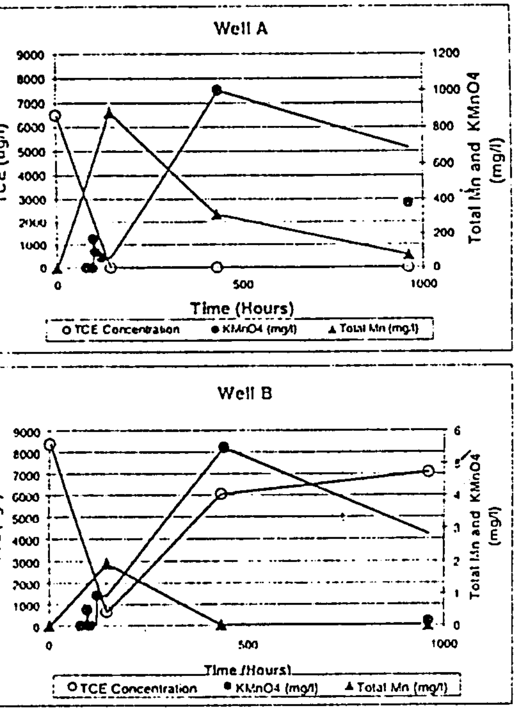
Permanganate injection tests that include a conservative tracer provide a means to evaluate the impact of reactive transport on the overall permanganate distribution. Figure 1 shows the results of a combined permanganate-tracer injection test performed at the IDC Cape Canaveral, Florida demonstration project (Mott-Smith et al., 2000). In this test, 1.5 % to 2% KMnO4 was injected for 2.5 days with a 2 ppm sodium fluoride tracer. The fluoride tracer is conservative, and its distribution represents the transport of particles injected. The fluoride transport in this test was up to 20 feet and greatly exceeded the permanganate transport. Permanganate transport was especially limited toward the south (bottom of figure), where initial TCE concentrations in soils were as high as 5,000 mg/kg, compared to 100 mg/kg TCE north of the injection point.

The tracer test results are consistent with the rapid consumption of permanganate in the presence of high TCE concentrations (i.e. DNAPL). In comparison, at a site in Maine, where TCE concentrations in water were approximately 1,500 ppb, and DNAPL was not present, permanganate transport was observed over distances in excess of 100 feet.

PERMANGANATE-CONTAMINANT REACTION KINETICS

The kinetics of reactions between permanganate and contaminants are obviously an important factor in the overall treatment success obtained. Huang, et al. (1999) showed that oxidation of TCE by KMnO4 was second order, with a fast second order rate constant of .083 +/- 0.05 M^{-1} s^{-1}. This rate constant applies to aqueous-phase reactions. Permanganate is essentially non-sorptive, while organic contaminants can exist in aqueous, sorbed, or NAPL phases. Permanganate-contaminant reactions occur in the aqueous phase, and NAPL and sorbed phases must be treated either by interfacial contact with the aqueous phase, or by mass transfer to the aqueous phase. The objective of this section is to consider the dynamics of permanganate-contaminant reactions, in terms of the presence and disappearance of reactants and products as well in terms of chemical equilibrium between contaminant phases.

An interesting observation from numerous field sites is that significant dissolved contaminant concentrations are generally not observed in the presence of aqueous permanganate. Figure 2 illustrates the breakthrough and



gure 2. Dissolved TCE, KMnO4, and total
n at two wells During a Field Pilot Test.

disappearance of permanganate in two monitoring wells at a site in Australia. Data from Wells A and B both show that Dissolved TCE levels are suppressed by the presence of permanganate. At Well A, TCE levels do not rebound, while at Well B TCE levels do rebound. This indicates that at Well A, a sufficient mass of permanganate was delivered to treat dissolved, and sorbed TCE, whereas at Well B, sorbed TCE was not completely oxidized. The untreated sorbed TCE mass at Well B provided the source of TCE mass transfer into the aqueous phase, as permanganate was consumed. Rebound of dissolved contaminant levels is common to field pilot tests, where the permanganate mass added may not achieve complete treatment. In many cases, full
ale treatment is implemented in phases, with later phases focused on areas of
eatest rebound. In this manner, the ultimate permanganate dose can be
livered most efficiently to the specific zones requiring treatment. This
proach may be more cost effective than detailed characterization of the spatial
riability of permanganate demand prior to treatment.

The total dissolved Mn shown in Figure 2 may include (1) dissolved
nganese available from MnO_4^- ion, (2) manganese-containing intermediates
ch as cyclic esters (i.e. $MnO_4C_2HCl_3$) and $HMnO_3$, and (3) dissolved Mn^{2+}
rived from MnO_2. Figure 2 indicates that total dissolved manganese goes
ward zero as permanganate is consumed. This indicates that the measured
solved Mn represents primarily (1) and (2), and that little or no dissolved Mn is
rived from MnO_2. This is expected, since MnO_2 is a solid-phase colloidal
ecipitate, with very low aqueous solubility.

ATRIX INTERACTIONS AND GEOCHEMICAL EFFECTS

Relevant matrix interactions and geochemical effects involved in in-situ
idation using permanganate include matrix oxidant demand, oxidation of native
etals in soils, and changes in overall groundwater geochemistry related to redox
ate and ion exchange related to addition of Na^+ or K^+ with the permanganate salt

The overall permanganate consumption required to achieve contaminant treatment is the sum of permanganate demand from contaminant oxidation and matrix oxidant demand. Matrix oxidant demand refers to the oxidant consumption that can be attributed to background soil and groundwater conditions. Matrix demand can be derived from oxidation of natural organic matter, reduced metals, carbonates, sulfides, etc. Matrix demand can be highly variable, depending on background geochemical conditions, and is also highly dependent on permanganate solution concentration (R. Siegrist, pers. comm.), since permanganate reaction rates are second order.

Overall permanganate demand rates (i.e. contaminant demand plus matrix demand) across multiple sites have ranged from a few grams of permanganate per kg of soil (clean sands with dissolved contaminants) to as much as several hundred grams permanganate per kg of soil (organic clays containing non-aqueous phase liquid (NAPL) and 6% organic carbon content). In some cases, the overall permanganate demand may be driven more by matrix demand than by contaminant demand.

Oxidation of native metals in soils represents not only a source of matrix demand, but also potentially a mechanism by which groundwater quality can be degraded. The primary metals of concern include chromium, uranium, vanadium, selenium, and molybdenum. They may exist naturally in a chemically reduced, insoluble state at a particular site, and therefore not be detected in groundwater. However, because they are more soluble under oxidizing conditions, these metals can be mobilized by in-situ oxidation. Sites where this could be a potential problem can include sites where naturally occurring metals concentrations in soils are elevated, or sites where historical metals contamination was attenuated by natural chemical reduction processes. In such cases, it is desirable that natural geochemical conditions will attenuate the metals. Natural attenuation mechanisms can include sorption and chemical reduction back to an immobile valence. Metal sorption may occur at a range of different sites, including iron hydroxides, organic carbon, and MnO_2 produced by permanganate oxidation reactions.

The most commonly observed mobilization of metals is oxidation of Cr 3+ to Cr 6+. Preliminary data indicates that there is a strong correlation between total pre-treatment chromium concentrations in soil to the tendency to mobilize dissolved chrome during permanganate treatment. Table 1 shows data from three sites where elevated background chromium concentrations resulted in liberation of dissolved Cr6+. In all three cases, the dissolved chromium attenuated over time. Sites with background chromium in soils of less than about 5 mg/kg have not resulted in liberation of dissolved Cr6+ upon oxidation treatment.

Figure 3 shows the time trend of dissolved chromium for Site B (Table 1). Site hydrogeologic data and monitoring of surrounding wells indicated that the chromium attenuation is a result of a combination of sorption and chemical reduction and not attributable to dilution. The dissolved chromium half-life in this case was 6 days

Table 1. Lab and Field Data on Chromium Liberation and Attenuation.

Site	Lab/ Field	Pretreatment Total Cr in soil (mg/kg)	Maximum Dissolved Cr6+ Liberated (mg/l)	Cr6+ Attenuation Observed?
A	Lab	368	105 mg/l	Yes, 40 mg/l per pore volume of soil contact
B	Field	65	3 mg/l	Yes, to 0.007 mg/l in the field after 45 days
C	Field	28-94	1.5 mg/l	Yes, to 0.15 mg/l after 23 days

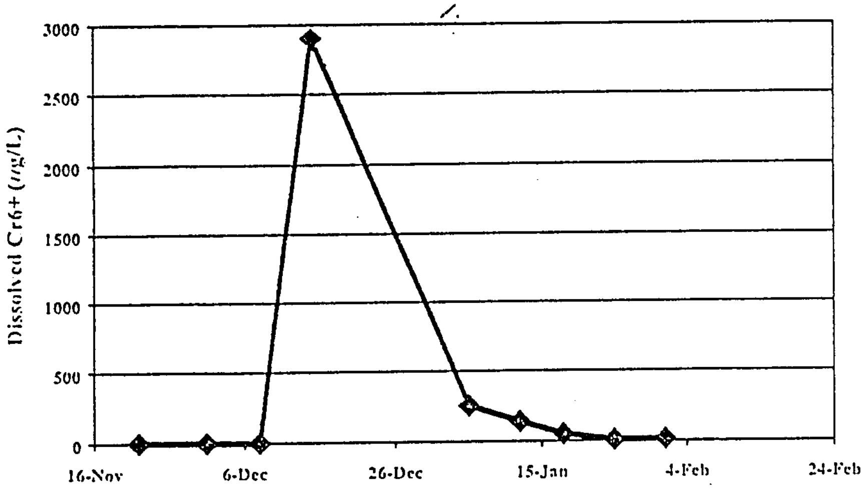


Figure 3. Time-Series plot of dissolved Cr 6+ attenuation after permanganate treatment.

Permanganate oxidation can induce changes in overall groundwater geochemistry by influencing the redox state, and by inducing ion exchange. Oxidation reduction potential (ORP) values during in-situ permanganate treatment are typically > 200 mv within the zone of active treatment.

The addition of high concentrations of K^+ or Na^+ with the permanganate salt, can impact ion exchange for both cations and anions. For example, following $KMnO_4$ addition, cations such as Mg^{2+} and Na^+ are commonly observed to increase as a result of cation exchange with K^+. Anion concentrations can increase following $KMnO_4$ or $NaMnO_4$ addition, because as the MnO_4^- reacts, a net positive charge imbalance results, that can be offset by anion desorption

CONTAMINANTS TREATED AND REDUCTIONS ACHIEVED

A wide range of contaminant types and concentrations have been subjected to in-situ oxidation using permanganate. Table 2 summarizes the combined lab and field results from multiple sites, many involving contaminant mixtures. These results show that while permanganate can treat a wide range of recalcitrant organics, not all organics can be treated effectively. Since permanganate is a weaker oxidant than ozone, hydrogen peroxide, or hydroxyl radical, these other oxidants may more be applicable to some of the more difficult to treat compounds listed here. Conversely, for the contaminants that are readily treated by permanganate, its stability and persistence in the subsurface facilitate advective and diffusive oxidant transport, potentially improving the overall lev of treatment obtained.

Table 2. Summary of Contaminant Treatment Results in Lab and Field

	Maximum Percent Treatment Achieved for Various Starting Contaminant Levels		
Contaminant	Low Level Dissolved	High Level Dissolved/Sorbed	NAPL
chlorinated ethenes (PCE, TCE, DCE)	>99%	>99%	>99%
chlorinated ethanes (TCA, DCA)	>99%	40%	n.a.
vinyl chloride	>99%	n.a.	n.a.
chloroform	0%	0%	n.a.
methylene chloride	0%	0%	n.a.
carbon tetrachloride	0%	n.a.	n.a.
CFC 113	0%	0%	n.a.
toluene, xylene	>99%	n.a.	n.a.
benzene, ethylbenzene	30%	20%	n.a.
C6-C9 TPH	70%	50%	n.a.
C10-C14 TPH	0%	0%	n.a.
C15-C28 TPH	0%	0%	n.a.
Pentachlorophenol	>99%	>99%	n.a.
benzo(a)pyrene, and other PAHs	>96%	>96%	n.a.
MTBE	>99% *	>99% *	

notes: 1) n.a. – data not available
2) all data expressed as > represent treatment results below detection limits
3) * - MTBE transforms to tert-butyl alcohol (TBA), which does not degrade in the presence of permanganate.

SUMMARY AND CONCLUSIONS

In-situ chemical oxidation is an emerging remediation technology that shows great promise, but is not a "silver bullet" for treatment of all sites. Successful implementation of in-situ oxidation requires favorable oxidant-contaminant kinetics, delivery of an adequate mass of oxidant, and effective subsurface oxidant delivery and transport. While this paper has not dealt with hydrogeologic factors, ultimately geologic conditions may largely dictate success or failure at a given site.

Permanganate is highly effective for treatment of some compounds, such as chlorinated ethenes, marginally effective for others such as chlorinated ethanes, and somewhat ineffective on some contaminants such as benzene. Permanganate has been found effective for treatment of dissolved, sorbed, and NAPL contamination. Since treatment of NAPL requires a larger oxidant dose, all relevant performance criteria and design issues become more critical.

Many of the general observations and performance criteria that apply during in-situ chemical oxidation using permanganate also apply to other in-situ oxidants, including ozone and Fenton's reagent. We have attempted in this paper to avoid direct comparisons between oxidant performance. The reader is encouraged to critically examine the potential strengths and weaknesses of all in-situ oxidants.

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A FIELD DEMONSTRATION OF TRICHLOROETHYLENE OXIDATION USING POTASSIUM PERMANGANATE

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Abstract: A multi-year demonstration of in-situ oxidation using a solution of potassium permanganate is ongoing at the U.S. Army Cold Regions Research and Engineering Laboratory (Hanover, New Hampshire). Consistent with the Laboratory's mission to provide solutions for cold-related problems, chemical oxidation was selected to evaluate a low-cost alternative to bioremediation in cold climates. Mean annual temperature at the Hanover site is 7 °C. Treatment began in August 1999 and is expected to continue through at least part of 2001. Oxidant is delivered to unsaturated soils about 30 m above the water table in regions that contained residual-phase trichloroethylene (TCE). Treatment progress is monitored through periodic collections and analyses of the solid, liquid, and gas matrices within the treated volume. Here, an assessment of oxidant distribution in the heterogeneous formation is presented in the context of initial site conditions, treatment methodology, and preliminary results. Observations of permanganate distribution in post-treatment soil samples illustrate the importance of site characterization for improving the operational efficiency of an oxidative treatment system.

INTRODUCTION

Variably saturated, heterogeneous, low-permeability soils are challenging media for removal of sorbed organic contaminants. In settings of contrasting permeability, contaminants may accumulate above lower permeability strata, facilitating migration into areas otherwise inaccessible due to diffusion kinetics. Because of its characteristic stability in media that contain low levels of natural organic matter and reduced mineral species, potassium permanganate ($KMnO_4$) has the potential to access and to treat contaminated soils in transport-limited conditions.

Previous oxidation field studies have underscored the importance of a comprehensive, site-specific understanding of soil stratigraphy, soil properties, and contaminant distribution. One of the earliest field trials to evaluate soil treatment with permanganate was reported by Schnarr et al. (1998). There, $KMnO_4$ solution was injected over a period of several months into an aquifer containing residual sources of perchloroethylene (PCE). Noting horizontal bedding features on scale of millimeters to centimeters, it was concluded that the effectiveness of treatment with $KMnO_4$ depended strongly on non-aqueous-phase liquid (NAPL) distribution and its effects on dissolution. West et al. (1997) reported similar observations following permanganate injection within a heterogeneous aquifer conmeated by $KMnO_4$, but oxidant distribution appeared to be the controlling factor for overall remediation.

NAPL Oxidation in the Vadose Zone. Because $KMnO_4$ is delivered in solution, NAPL must be transferred to the solution for oxidation to occur. This process of dissolution depends strongly on the interfacial area between the non-aqueous and aqueous phases. The pore-scale spatial characteristics of a NAPL in two- and three-fluid porous systems are a consequence of many factors, including wetting behavior, spreading coefficient, fluid saturation ratios, and the discrepancy (between two- and three-fluid systems) of forces resisting an infiltrating NAPL. Scanning electron microscopy has revealed fundamental differences in the distribution of NAPL within two- and three-fluid systems. In a three-fluid soil system, Hayden and Voice (1993) observed continuous NAPL distribution, including pendular rings and films. Wilson et al. (1988) observed isolated NAPL globules in a two-fluid system characteristic of capillary entrapment, and interconnected NAPL films between water and air phases and within the air phase in three-fluid systems.

The net result of these contrasting spatial configurations can be a larger ratio of NAPL surface area to volume in unsaturated (versus saturated) conditions as demonstrated in qualitative experiments with PCE (Schwille, 1988). Consequently, unsaturated pores may provide larger interfacial areas between phases, enabling aqueous oxidation of residual NAPLs to be particularly effective in the vadose zone. Additionally, one may anticipate improved efficiency with oxidant distribution in the vadose zone owing to lesser $KMnO_4$ dilution with existing groundwater and the presence of capillary forces to facilitate oxidant migration in zones of reduced hydraulic conductivity.

TCE Oxidation by Permanganate. As potassium ion (K^+) is non-reactive in aqueous solution, reduction of the permanganate ion (MnO_4^-) is considered here. In the presence of reducing agents, the oxidation state of manganese is determined by the solution pH (Stewart, 1965). In basic or neutral aqueous solutions, the manganese precipitates as manganese dioxide (MnO_2), which is also a strong oxygen transfer agent:

$$MnO_4^- + 2H_2O + 3e^- \quad MnO_2\,(s) + 4OH^-. \tag{1}$$

Acidic solutions can reduce MnO_4^- to the manganese ion (Mn^{2+}):

$$MnO_4^- + 8H^+ + 5e^- \quad Mn^{2+} + 4H_2O. \tag{2}$$

Based on laboratory observation, mass balance and redox requirements, Schnarr (1992) proposed the following reaction equation for $KMnO_4$ and TCE:

$$C_2Cl_3H + 2\,KMnO_4 \quad 2\,MnO_2(s) + 2\,CO_2 + 2KCl + HCl \tag{3}$$

in which six electrons are transferred from carbon to manganese atoms per molecule of TCE.

Huang et al. (1999) confirmed the stoichiometry of Equation 3 based on measurements of consumption for $KMnO_4$ and TCE and determined a second order rate constant of 0.89 $M^{-1}s^{-1}$ at 20°C. Yan and Schwartz (1999) calculated a second order rate constant for TCE of $k = 0.67\ M^{-1}s^{-1}$. The authors determined that pH in the range of 4–8 did not affect the rate of TCE disappearance but noted that decomposition of a cyclic complex was highly pH dependant, with competition for reaction among MnO_4^- and OH^- ions.

Site Description. In-situ treatment of vadose-zone soils is applied at two separate source areas as part of an overall approach to address TCE contamination in the groundwater at the Hanover, NH, location. These sites, separated by a distance [illegible] about 50 m, are identified as Areas of Concern 2 and 9 (AOC 2 and AOC 9). T[illegible] source at AOC 2 was a leaking underground storage tank that was removed in 1972. TCE contamination at AOC 9 is attributed primarily to accidental surface spills during the 1970s and 1980s.

Each site encompasses an area of approximately 300 m^2. The majority of TCE is found within the first 10 m below the ground surface. Water table depth is approximately 40 m. Pre-treatment estimates of TCE mass, based on nearly 700 combined samples, indicated approximately 2500 and 2000 kg at AOC 2 and 9, respectively. However, additional samples collected during treatment at AOC 9 suggest that these initial estimates may have been low. The lacustrine sediments at both sites are stratigraphically similar, and contain comparable contaminant distribution profiles, owing to a pattern of inter-bedded clay lenses within a predominantly silt formation. Large numbers of particle size analyses were performed to map field-scale heterogeneity. The results indicated that both sites, taken as a whole, have nearly identical compositions consisting of 81% silts, 12% clays, and 7% sands. Because of these similarities and the limited space that is available here, only data from AOC 9 are presented hereafter.

Soils within the initial treatment zone at AOC 9, between 3.7 and 9.8[illegible] below the ground surface, consist of an average of 92.8% fines (< 0.075 mm) based upon analyses (ASTM D 1140-92) of 415 samples ($\sigma = 9.4$). The mean calculated porosity based upon analyses (ASTM D 4404-84) of 76 samples is 43.3% ($\sigma = 8.2\%$).

Background soil chemistry is summarized in Table 1.

TABLE 1. Background soil chemistry at AOC 9.

Analysis	Method	Mean	σ	Units	Sample Qty
potassium	3050/6010	1718.6	592.0	mg kg^{-1}	59
manganese	3050/6010	509.7	177.6	mg kg^{-1}	59
chloride (detected)	9251	94.1	145.9	mg kg^{-1}	37
chloride (non-detected)	9251	< 51		mg kg^{-1}	22
pH	9040/9045	9.0	0.7	pH	59
cation exchange capacity	9081	9.8	3.9	meq 100g^{-1}	59

Clay lenses within the silt formation, typically 4–10 cm thick, appear at regular intervals of several tens of centimeters. The highest concentrations of refound directly above many of these lenses (Table 2). Concentrations within and directly below the clay formations are often two and three orders of magnitude lower, respectively. These data appear to reflect years of diffusion of TCE across otherwise impermeable regions. As previously stated, $KMnO_4$ may also diffuse into these areas, owing to its stability, the corresponding kinetic processes of TCE dissolution and oxidation, and resultant increase in concentration gradients for both aqueous-phase TCE and permanganate (Schnarr et al. 1998).

TABLE 2. TCE in sub-samples of soil cores obtained from AOC 9.

Core I.D.	Sample Depth (cm)	Soil Classification	TCE (mg kg^{-1})
5-1	528	silt	48,900
5-1	533	clay	574
5-1	543	silt	57
5-2	586	silt	34,800
5-2	591	clay	459
5-2	601	silt	23
6-2	583	silt	61,000
6-2	588	clay	517
6-2	598	silt	16
6-3	645	silt	38,000
6-3	650	clay	311
6-3	655	silt	92

MATERIALS AND METHODS

Construction and Operation. The in-situ soil treatment system consists of an oxidant mixing plant, two satellite buildings to manage distribution to individual wells, and 32 injection wells (as of this submission). A material-flow schematic is shown in Figure 1. Currently, batch mixtures consist of 75 kg $KMnO_4$ and 5000 L of water (1.5% $KMnO_4$). Operating capacity at the present concentration is 400 kg of $KMnO_4$ per day, though lower delivery rates are normally applied. Solution flow rate to individual wells is typically 4–6 L min^{-1} (1–1.5 g s^{-1} of $KMnO_4$) at pressures ranging from 0.5–1 bar. Both source areas are treated simultaneously with each site having one injection point in use at any given time. A system of air-actuated valves is programmed to sequentially step through the injection arrays at pre-set intervals.

Permanganate solution is delivered to the subsurface through an array of 5.1-cm-diameter well screens placed inside 7.6-cm-diameter boreholes (Figure 2). Each well screen is 1.2 m long and isolated above by an inflatable borehole packer that enables delivery of the oxidant under pressure. All near-surface piping s buried beneath insulation board and contains internal heat tracer for freeze proection.

The permanganate mixing plant houses two 11,300-L solution tanks, two gravimetric screw feeders with hoppers, an overhead crane for material handling, a ventilation and dust control system, a wash area for cleaning used drums and equipment, emergency and personal protection equipment, controls, alarms, and

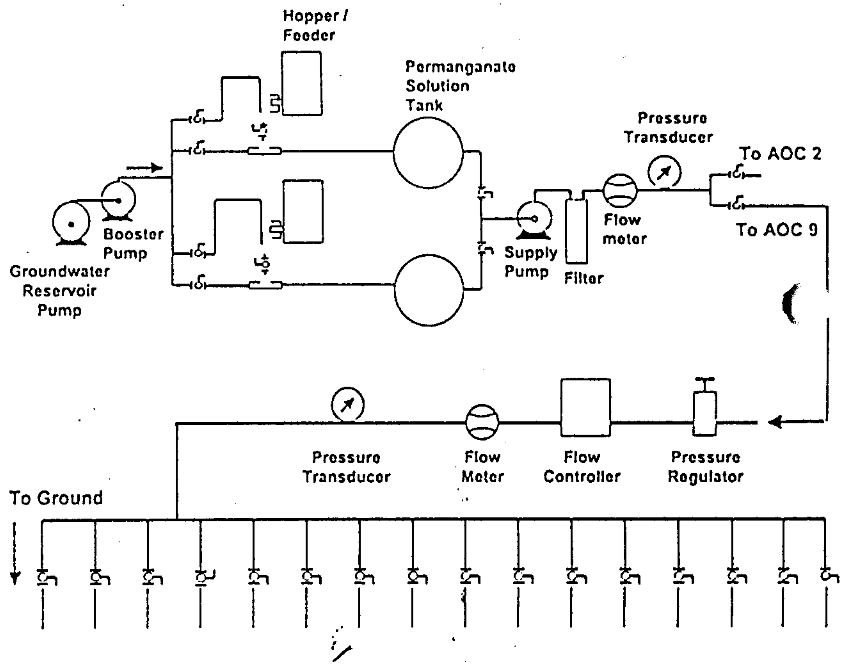
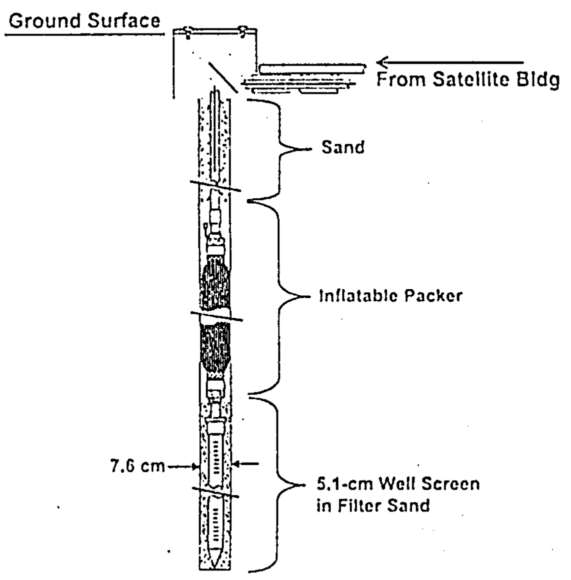


FIGURE 1. Material flow schematic.



structed in duplicate to allow simultaneous batch preparation and consumption. Material flow processes including rates, pressures and temperatures are monitored within the oxidant mixing plant and each satellite distribution building. All aboveground material handling hardware, at both the mixing plant and the satellite buildings, is completed within lined containment walls to prevent surface spills to the environment.

Site Monitoring. The primary measures of treatment progress are visual inspection of soil cores for evidence of $KMnO_4$ permeation and analyses of soil samples to determine TCE concentrations. Lysimeters, soil gas implants, and neutron moisture probe access pipes were installed to monitor secondary effects including pore water chemistry, soil gas composition, and moisture distribution.

Soil samples are collected using a 2.5-cm direct-push sampler. Continuous profiles are collected at 0.6-m intervals, and then subdivided to 0.3-m lengths. Each section is split along the length of the sample to produce quarter sections of the original core. Half of each 0.3 m section is preserved in HPLC-grade methanol for laboratory analysis. A small quantity of sodium thiosulfate is added to the methanol to reduce any permanganate present in the sample. The remainder of soil is used to determine moisture content and to perform additional analyses.

RESULTS AND DISCUSSION

In the alkaline soil environment of AOC 9 (see Table 1), $MnO_2(s)$ will precipitate during the reduction of MnO_4^- per Equation 1. For soil density of 1.4 g mL^{-1}, soil porosity of 0.43, and $MnO_2(s)$ density of 1.2 g mL^{-1}, the hypothetical maximum pore volume reduction by $MnO_2(s)$ is 0.36% per 1000 mg kg^{-1} of TCE. In regions having TCE concentrations of several tens of thousands of milligrams per kilogram (see Table 2), localized reductions in permeability may be significant. Schnarr (1992) measured a decrease in pore volume of 5.6% following injection of $KMnO_4$ into a PCE-contaminated soil, compared to 1% volume change attributed to the contaminant. As NAPL occupies a specific range of pore sizes determined by initial moisture content (Schaefer et al., 1999), the pore-scale distribution of the $MnO_2(s)$ may be more important than quantity if accumulations in pore throats weaken pore connectivity. Mercury intrusion tests on soils containing extensive MnO_2 staining are thus far inconclusive as to changes in pore size distribution.

Soil cores containing unreduced $KMnO_4$ and MnO_2 staining on TCE-contaminated soil provide visual evidence of $KMnO_4$ migration pathways. Permeated soils that contained high initial concentrations of TCE are indicated by dark brown discolorations caused by accumulation of MnO_2. The intensity of discoloration is assumed to be comparative to the amount of MnO_2 and hence is a visual indicator of original TCE distribution. Figure 3 shows a section (6.5- to 6.7-m depth) from a 2.5-cm soil core collected approximately 1 m from an injection well (4.1- to 5.3-m depth) following the addition of 200 kg $KMnO_4$. Dark brown staining directly above a clay lense indicates TCE distribution characteristic of that found in Table 2. The sample described in this example contained a composite average of 1900 mg kg^{-1} TCE—less than the 5700 mg kg^{-1} of a neighboring sample collected prior to treatment. $KMnO_4$ did not appear to have permeated the clay layer. As previously suggested, the stability of $KMnO_4$ may enable passive, long-term treatment of the clay soil because of the parallel diffusion processes of TCE and $KMnO_4$. Inspection of numerous other samples (not shown) found $KMnO_4$ permeation through veins of relatively course-grained material between layers of finer material. Isolated layers of light brown staining caused by MnO_2, bordered above and below by thin layers of dark brown staining, suggest $KMnO_4$ permeation through the heterogeneous formation may have followed discrete pathways preceded by TCE.

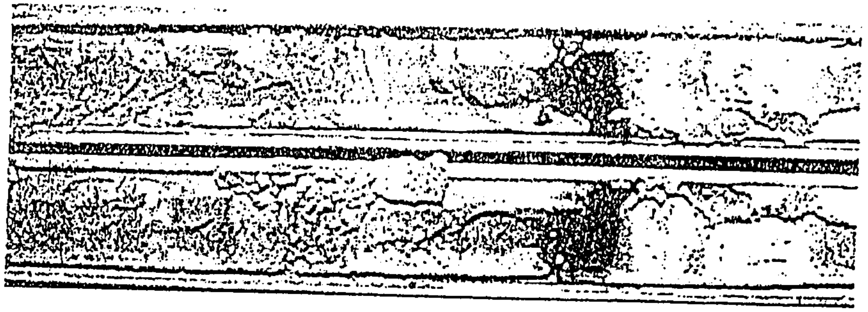


Figure 3. 2.5-cm-diameter soil core collected near AOC 9 injection well. Depth shown is 6.5–6.7 m (left to right). Section to the left of dark band showed light purple to brown discoloration, indicating $KMnO_4$ permeation and light oxidation. Dark band indicated extensive oxidation in area where TCE was concentrated above clay lense.

Preliminary results indicate that regions of relatively low initial TCE concentrations can be effectively treated if flooded by $KMnO_4$ solution. Areas within AOC 9 that contained TCE concentrations on the order of ten to hundreds of milligrams per kilogram were treated to levels near or below the detection limit of about 100 µg kg^{-1} following single events of intensive $KMnO_4$ additions to nearby injection wells. However, mass balance estimates and initial results indicate that areas containing TCE concentrations on the order of several thousand milligrams per kilogram will require extensive and prolonged applications of $KMnO_4$ treatments. For optimum efficiency, the rate of these applications should not greatly exceed the rate of TCE dissolution. Consequently, we are modifying our approach to oxidant delivery in these areas to include low-flow, direct-push injection points that will enable localized control of oxidant distribution.

CONCLUSIONS

Preliminary analytical data and inspection of post-treatment samples have highlighted the importance of site characterization for proper design of efficient in-situ oxidative treatment systems. Post-treatment soil cores provided visual evidence that $KMnO_4$ permeation through the vadose zone might often have traced isolated paths of TCE migration. In areas with relatively low TCE concentrations, broad, nonspecific application of $KMnO_4$ appears to be effective. Regions of concentrated NAPL will require contaminant delineation and localized delivery.

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PASSIVE DESTRUCTION OF PCE DNAPL BY POTASSIUM PERMANGANATE IN A SANDY AQUIFER

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ABSTRACT: A drive-point tool for injecting reactive fluids into permeable sandy aquifers was developed and tested for in-situ remediation of contamination from a previous PCE DNAPL experiment in a shallow unconfined sand aquifer. The goal of this approach is to inject aqueous reactive chemicals such as potassium permanganate ($KMnO_4$) under moderate pressures (400-600 kPa) over a short time period, targeted at multiple depths in a borehole to create stacked coalescing treatment zones. Additional coverage is accomplished using multiple boreholes. The injections may be repeated periodically at intervals of 2 to 3 months until the desired degree of in situ treatment is achieved. Two separate injection episodes were conducted in which 14.7 kg of $KMnO_4$ were delivered in 860 L of solution. The monitoring showed that the distribution of $KMnO_4$ reached over 1.37 meters away from the injection points and that most of the consumption of $KMnO_4$ occurs within 2 months. Results suggest that the direct-push tool is time-efficient and effective for distributing reactive solutions. Diffusion and density driven advection, both sinking and spreading along lower permeability layers, further enhance the ability to deliver $KMnO_4$ into zones where DNAPL persists.

INTRODUCTION

Persistent plumes of dissolved chlorinated solvent contamination in sandy aquifers are common due to subsurface accumulations of dense non-aqueous phase liquids (DNAPLs). For permanent aquifer restoration the DNAPL must be removed or destroyed in-situ. One approach for in-situ destruction of chlorinated ethenes is chemical oxidation using potassium permanganate ($KMnO_4$), which was first studied by Schnarr and Farquhar (1992). Schnarr et al. (1998) showed the effectiveness of $KMnO_4$ for destruction of tetrachloroethylene (PCE) and trichloroethylene (TCE) in batch and column experiments using DNAPL mixed in sand, and in field experiments at Canadian Forces Base Borden, Ontario. Other investigators reported encouraging results based on field trials (Hood et al., 1997; McKay et al., 1998; Siegreist et al., 1999).

For sandy aquifers and some types of aquitards, an alternative to the use of recirculating forced-advection for the delivery of dissolved $KMnO_4$ to DNAPL zones is the inject-and-leave approach (Parker and Cherry, 1997). In this method, a high concentration $KMnO_4$ solution is injected rapidly into the DNAPL zone followed by a long period during which the $KMnO_4$ redistributes with no repeated injection until the oxidation by $KMnO_4$ ceases. For this study a direct-push drive-point tool for $KMnO_4$ injection at discrete depths was developed to deliver the $KMnO_4$ to useful distances radially from the injection point in the Borden aquifer.

The 9 x 9 m sheet pile cell used in this study at Canadian Forces Base Borden, was utilized previously for a geophysical experiment to evaluate the effectiveness of several different geophysical techniques for observing the movement and distribution of dense immiscible-phase organic solvents in the subsurface (Brewster et al., 1995). In 1991, 770 L of PCE, dyed red using the hydrophobic dye Sudan IV, were released in the 9 x 9 m cell. The DNAPL formed layers distributed from 1 m depth to the bottom of the aquifer at 3.5 m. In subsequent months, 425 L were removed by pumping 5 cm diameter wells at the bottom of the aquifer (Morrison, 1998). Soil vapor extraction (Flynn, 1994) and air-sparging (Tomlinson, 1999) removed part of the PCE in the aquifer, however an estimated 185-275 L of DNAPL remain inside the cell, primarily in the bottom meter of the aquifer and at the aquifer-aquitard interface (Morrison, 1998; Nelson, 1999).

The layered nature of DNAPL distribution makes many remediation schemes ineffective or inefficient because treatment chemicals transported by advection can circum-navigate lower permeability zones where much of the mass is present. Clean-up times will be long because mass transfer rates of contaminant and oxidants will control the time frame for destruction. The Drive Point Delivery System (DPDS) was designed to deliver a reactive chemical solution close to these discrete DNAPL layers within the aquifer. The goal is to inject the chemical reactant at targeted depths to distribute the $KMnO_4$ solution in discs that radiate away from the injection hole into the DNAPL zones. After the injection, diffusion and density-driven advection of the $KMnO_4$ solution provides more contact between the reactive chemical and the DNAPL mass.

To achieve maximum solvent mass destruction from each injection episode, the injected solution must be at or near the $KMnO_4$ solubility limit of 64 g/L at 20°C (Perry et al., 1984). A $KMnO_4$ solution at or near the solubility limit has a density relative to distilled water of approximately 1.03. Schincariol and Schwartz (1990) used laboratory sand tank experiments with NaCl solutions with relative densities in the range of 1.001 to 1.02 to study density driven advection. In a tank with layered permeable media they found that changes in hydraulic conductivity from $K_1=2.5 \times 10^{-5}$ to $K_2=1.4 \times 10^{-5}$ m/s, caused a 10 000 mg/L solution of NaCl to flow through the higher permeability layer then mound on the ower permeability layer. By analogy to these experiments, it is expected that igh concentration $KMnO_4$ solutions, 25 to 50% $KMnO_4$ saturation with densities n the range of 1.01 to 1.02, will sink and have a strong tendency to spread aterally along the top of sediment layers with slightly lower permeability. In the x 9 cell the hydraulic conductivity of the aquifer ranges between 4×10^{-3} to $4 \times$ 0^{-7} m/s.

The second transport mechanism relied upon is aqueous diffusion of the eactants. Rapid solvent destruction rates ensure high concentration gradients to rive diffusion at the $KMnO_4$-contaminant interface. In the field experiment resented here, the changes in $KMnO_4$ distribution caused by the combined influences of density and diffusion were monitored using a dense network of multi-level groundwater samplers and subsamples from continuous cores. The aquifer is fully saturated however no groundwater flow occurs inside the sheet pile cell except as a result of the injection of the dense aqueous $KMnO_4$ solution.

MATERIALS AND METHODS

Two $KMnO_4$ injection episodes were conducted in the unconfined Borden sand aquifer contained within a 9 x 9 m sheet pile cell keyed into an underlying clay aquitard, one in November 1997 and the second in July 1998 (Fig. 1). The injections were accomplished by driving a 7 cm long stainless steel, wire-wrapped well screen fitted to AW drill rod and connected to a 27 L pressure vessel (Drive-Point Delivery System, herein referred to as the DPDS). The injecti were made in a small experimental volume of the cell approximately 1.5 x 3 m in plan view situated in the bottom meter of the aquifer, 2.35 to 3.35 m depth. Two injection locations were used in each episode. In the first injection episode injections occurred at two depths at each location and in the second injection episode injections occurred at three depths at each location.

During the first injection episode, 5.7 kg of $KMnO_4$ were injected in 427 L of solution. The average injection rate was 3.8 L per minute at 470 kPa. The injection pressures varied between 380 and 515 kPa and rates between 3.5 and 4.5 L per minute. In the first hole, INJ-1, 99 L were released at 2.70 m depth, and 103 L at 3.30 m depth. In the second hole, INJ-2, 84 L were released at 2.70 m depth, and 98 L at 3.30 m depth. The rest of the 43 L of fluid was injected during the pushing of the injection tip to desired depths. The injection took approximately 8 hours including equipment setup and disassembly.

During the second injection episode, which took 7 hours, 9 kg of $KMnO_4$ were delivered in 429 L at an average injection rate of 3.7 L per minute, with pressures between 430 and 590 kPa. As in the first experiment two injectio holes were used within 30 cm from the first injection locations. In the first ho INJ-3, 104 L were released at 2.63 m depth, 90 L at 3.15 m depth, and 21 L at 3.35 m depth. In the second hole, INJ-4, 105 L were released at 2.50 m depth, 82 L at 3.15 m depth, and 39 L at 3.30 m depth.

Groundwater samples were collected from a detailed 3D sampling grid of multi-level samplers constructed out of 3.18 mm (1/8") tubing and analyzed for $KMnO_4$, chlorinated ethenes (PCE, TCE, and DCE), pH, Eh, and conductivity. Continuous cores were taken at 23 locations in 1.5 m long, 5 cm diameter aluminum tubes using a piston coring device (Starr and Ingleton, 1992). The cores were cut longitudinally and sampled at specific depths based on visual inspection for PCE and MnO_2 occurrence.

RESULTS AND DISCUSSION

Each injection episode created 4 $KMnO_4$ ellipsoids, two in the upper aquifer and two at the aquifer-aquitard interface. The ellipsoids in the upper aquifer had a diameter to thickness ratio of approximately 3. The ellipsoids created at the aquifer-aquitard interface had a larger diameter [illegible] diameter to thickness ratio of 4-5. The horizontally elongated nature of the $KMnO_4$ emplacements is most likely due to anisotropy in the aquifer hydraulic conductivity ($K_{horizontal} > K_{vertical}$). Falling head tests on repacked core segments, 5 cm long, show only minor K variability ($1x10^{-6}$ to $1x10^{-4}$ m/s) inside the cell (Fig. 1), however horizontal beds are visible at the mm to cm scale illustrating the scale of hydraulic conductivity variability.

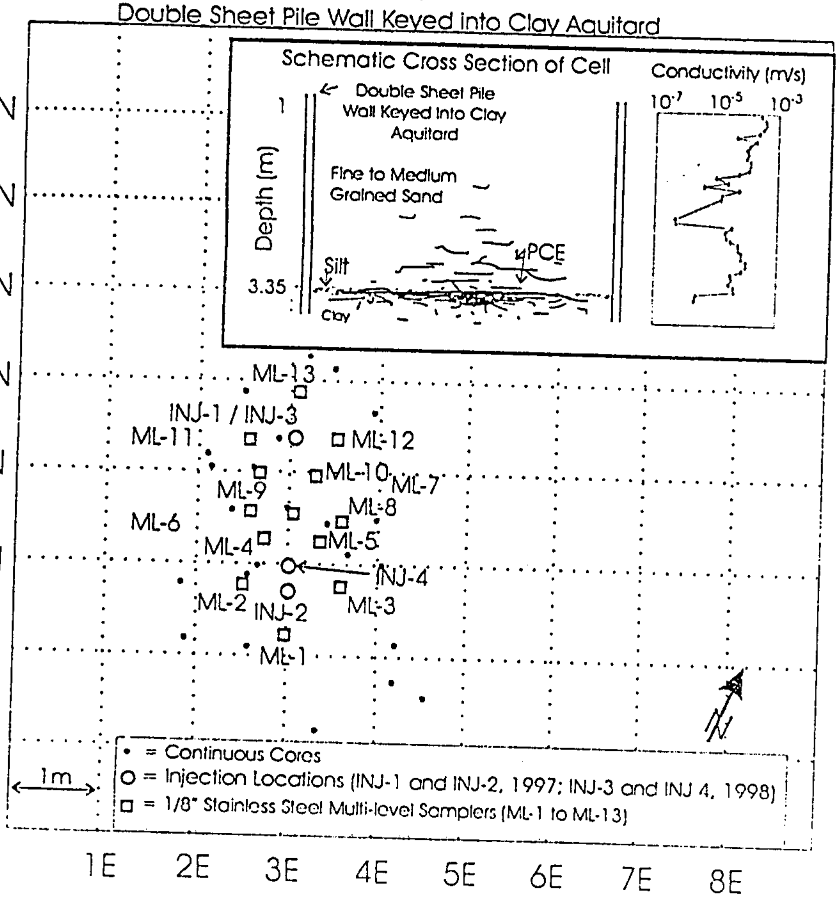

FIGURE 1. Plan and cross-section views of the 9 x 9 m cell and layout of the $KMnO_4$ experimental area. Each multi-level sampler is constructed of 1/8" diameter stainless steel tubes terminating at 11 depths vertically spaced 10 cm apart. INJ 1 and 2 were used in $KMnO_4$ injection episode 1 and INJ 3 and 4 in episode 2. A typical profile of permeability determined at a 5-10 cm sample interval by falling head permeameter shows the layering of the Borden aquifer.

Groundwater sampling showed post-injection movement of $KMnO_4$ in the quifer. Spreading of $KMnO_4$ was evident in 5 multi-level samplers and was ndicated by the arrival of $KMnO_4$ in some multi-level samplers at late time. In

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bundles 6, 8, 9, 10, and 12, $KMnO_4$ was absent at all sample depths until late time when it appeared at the 3.05 and 3.15 meter depths, the depth of the sand/silt interface. The $KMnO_4$ on the aquifer-aquitard interface spread laterally away from the injection hole locations with time (Fig. 2). The maximum coverage was at 23 days after the injections, coinciding with the arrival of $KMnO_4$ from the upper injection levels (Fig. 3). The spreading of $KMnO_4$ along the aquifer-aquitard interface enabled the treatment of soil up to a 1.37 m radius and with

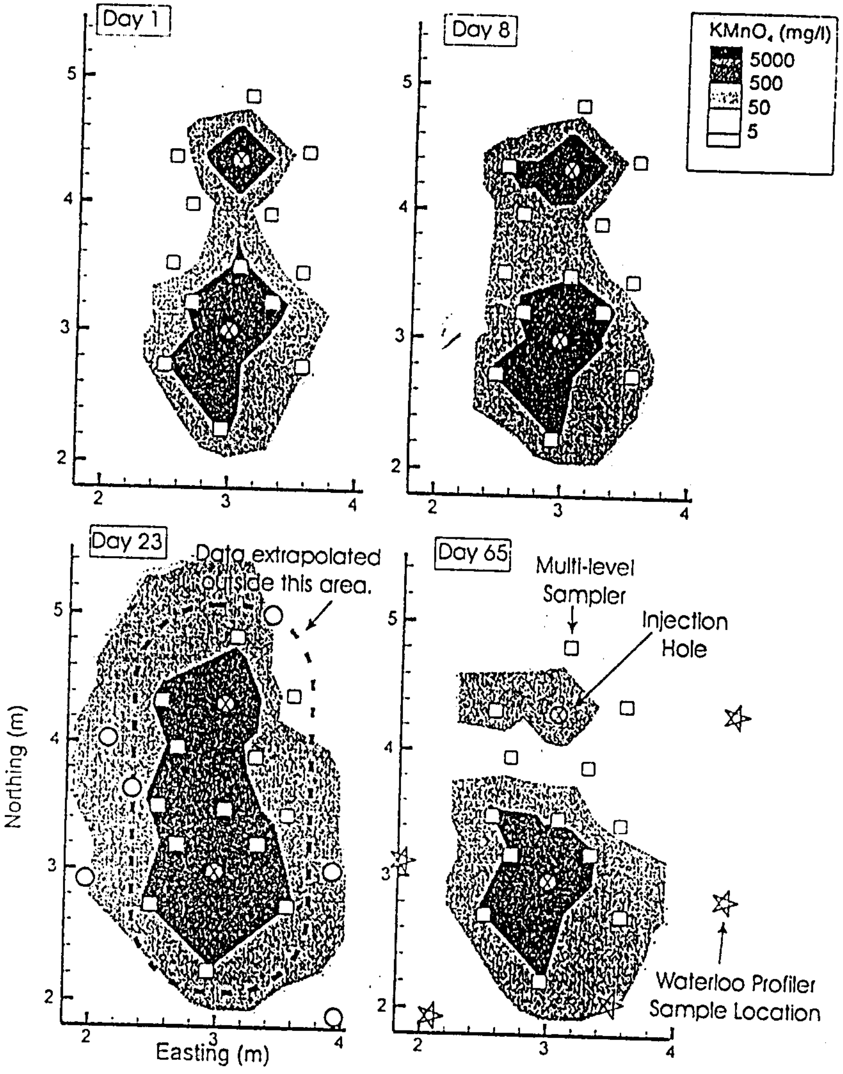

FIGURE 2. Plan view Distribution of $KMnO_4$ on the aquifer-aquitard interface (3.05 - 3.35 m depth) after the second injection episode. The contours are extrapolated beyond the multi-level samplers using data from soil cores (Day 101/102)

more complete coverage than in the overlying aquifer. Because prior to injection no groundwater flow occurred in the cell, the principal mechanism causing the post-injection migration of $KMnO_4$ on this time scale was density-driven advection.

As the $KMnO_4$ reacted with PCE, the Mn precipitated as Mn-oxide, and Cl^- was released from the destruction of PCE. The decline in MnO_4^- mass and Cl^- production of over time were measured in aqueous samples to track the reaction progress. By Day 85 MnO_4^- had decreased and chloride had increased from background levels of <10 mg/L to over 5000 mg/L which confirmed PCE destruction.

Cores taken after the injection episodes showed discrete layers of dark manganese precipitation at the mm to cm scale. These layers were most prominent, and appeared more consistently, above the silt layers at the aquifer-aquitard interface where layers of MnO_2 coatings ranged from 0.5 to 3 cm thick. These layers of extensive manganese precipitation reflect zones where PCE NAPL was initially present, indicating that the post-injection movement of $KMnO_4$ did contact DNAPL layers located above the finer-grained silt layers.

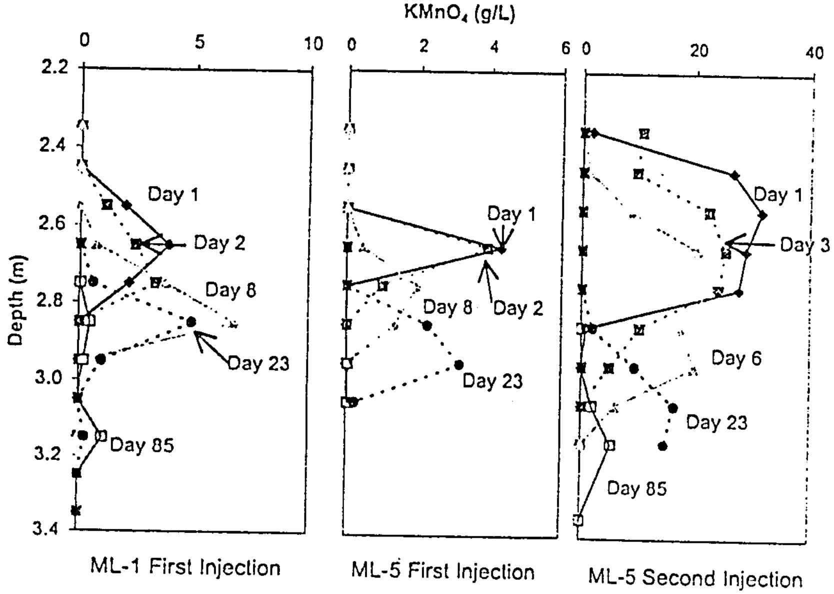

FIGURE 3. Evidence for $KMnO_4$ solution migration due to density effects based on downward progression of peak concentrations observed in multi-level samplers over time.

In the upper injection levels, in the absence of distinct silt or clay beds, the $KMnO_4$ migrated downward. In these zones the $KMnO_4$ ellipsoids descended through the aquifer gaining an additional 30 to 60 cm in diameter over a 60 cm vertical drop. Multi-level sampler profiles indicate the increase in depth of the peak concentration of $KMnO_4$ over time at a rate between 0.3 and 2.5 cm/d, with an average of 1.5 cm/d (Fig. 3). This density-driven advection maximizes the contact between $KMnO_4$ and the aquifer.

Schindcariol and Schwartz (1990) noted that the mounding of dense miscible fluids such as salt solutions on lower permeability units is similar to the behaviour of DNAPL. This post-injection re-distribution of $KMnO_4$, both downward migration and lateral spreading along lower permeability layers, allows the $KMnO_4$ to achieve contact with the DNAPL that resides at the bottoms of aquifers (Fig. 4).

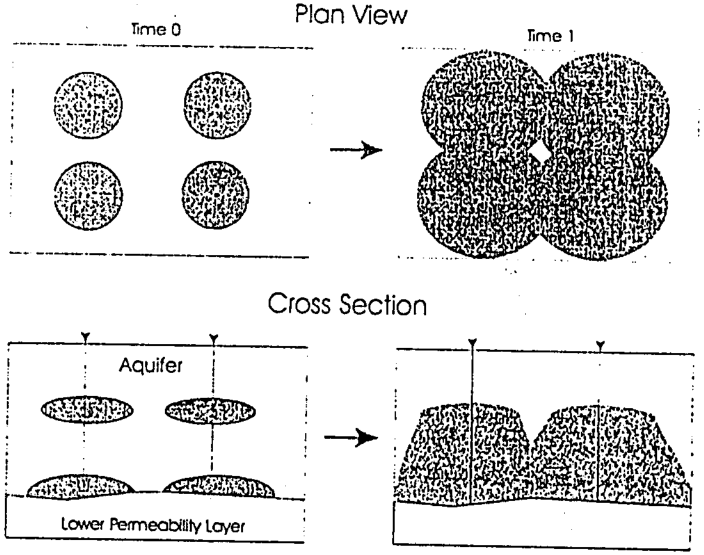

FIGURE 4. Conceptual representation of observations where solutions of $KMnO_4$ flow down and along lower permeability beds due to density-driven advection targeting the areas where DNAPL is most likely to exist.

CONCLUSIONS

During each injection episode 430 L of $KMnO_4$ solution were delivered to targeted areas over a period of 8 hours. The injections resulted in elliptical or disc-like emplacements of $KMnO_4$ that reached 1.4 m laterally from the injection points. Density flow caused the downward migration of $KMnO_4$ through the sand and lateral spreading along the silt layers at the aquitard-aquifer interface. This lateral spreading of $KMnO_4$ increased the volume of aquifer treated, especially along the silty beds. The redistribution of $KMnO_4$ resulted in treatment of a cylindrical volume of sand that extended 1 m radially from each injection hole.

The redistribution of the dense miscible $KMnO_4$ by density-driven advection during passive conditions is advantageous because it allows the $KMnO_4$ to contact the DNAPL situated along lower permeability layers at the bottom of the aquifer. Therefore, this injection method accomplished the delivery of $KMnO_4$ to targeted zones using minimal equipment and avoids continuous input, system operation and maintenance. Consequently, the inject-and-leave approach can result in reduced remediation costs.

Acknowledgements

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Experience with In-Situ Chemical Oxidation

Woodard & Curran has successfully remediated a wide range of contaminated properties using the *In-Situ Chemical Oxidation Technology*. We have effectively introduced potassium permanganate ($KMnO_4$) and hydrogen peroxide (H_2O_2) into the subsurface to destroy petroleum hydrocarbons, chlorinated solvents, and ammonia. Specifically, our experience using this technology includes:

- Open excavation application of potassium permanganate to subsurface soils and groundwater to remediate chlorinated solvents;
- Open excavation application of potassium permanganate to subsurface soils and groundwater to remediate ammonia;
- Injection of Potassium Permanganate through temporary drive points to remediate petroleum hydrocarbons in groundwater;
- Injection of Potassium Permanganate solution through an existing well matrix to address chlorinated solvents and other recalcitrant compounds in the aquifer;
- Injection of hydrogen peroxide/Fenton's Reactant through 2-inch diameter wells to remediate residual petroleum hydrocarbons in soils and separate phase NAPL floating on the surface of the water table; and
- Injection of hydrogen peroxide/Fenton's Reactant through 4-inch diameter wells to remediate residual DNAPL and dissolved chlorinated solvents present in the aquifer.

These activities have ranged from discrete application of potassium permanganate within a residential neighborhood to one of the first large-scale applications of potassium permanganate in the country of potassium permanganate at an EPA Region 1 Superfund site. The applications of potassium permanganate have included "soil mixing" approaches to address soil contamination, "inject and leave" approaches for cost effective, low impact polishing of an aquifer, and an aggressive "inject and control" approach to enhance the operation of an existing groundwater pump and treat system.

W&C's technical know how, scientific experience and hands-on experience with this technology allows us to design, permit and document the application of in-situ chemical oxidation technology in a successful, efficient and safe manner, regardless of whether it's a small scale polishing step or a comprehensive, high profile remediation project.

In addition to our remediation services, W&C's varied industrial, regulatory and hazardous waste experience will also be on-hand, to handle any and all technical, regulatory and risk issues that may arise during project activities. The remainder of this section presents case studies that describe in more detail our experience with in-situ chemical oxidation. Section 4 presents examples of our experience with other hazardous waste services.

SUCCESSFUL IN-SITU OXIDATION OF C_5 to C_{12} RANGE PETROLEUM HYDROCARBONS USING POTASSIUM PERMANGANATE

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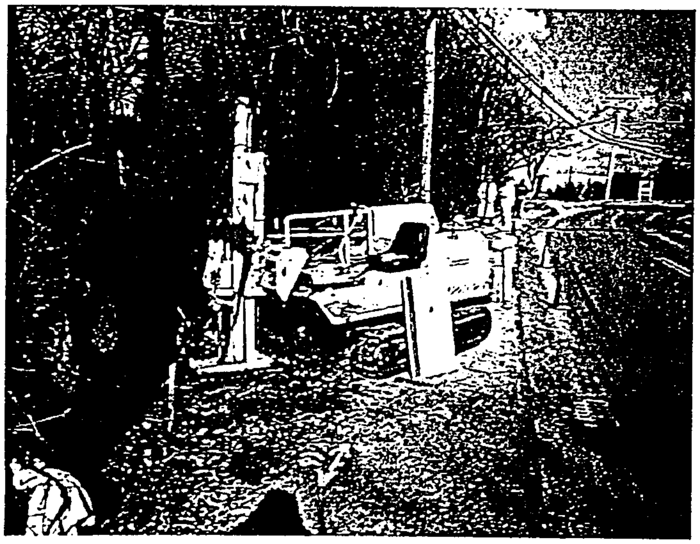
(Submitted to The First International Conference on Oxidation and Reduction Technologies for In-Situ Treatment of Soil and Groundwater, June 2001)

Passive injection of potassium permanganate was successfully utilized to remediate C_5 to C_{12} range petroleum hydrocarbons dissolved in the groundwater adjacent to a former jet fuel pipeline. Although in-situ oxidation of this range of petroleum hydrocarbons using potassium permanganate is not typically completed, this remedial approach was undertaken after analysis of site- and contaminant-specific conditions. Post-remediation monitoring indicates the potassium permanganate oxidation destroyed approximately 40% to 80% of the total volatile petroleum hydrocarbons present within the aquifer.



Subsurface investigation adjacent to the former jet fuel pipeline identified the presence of volatile petroleum hydrocarbons within an approximately 10,000-square foot groundwater plume. Groundwater occurs within a fine sand approximately 9 to 11 feet below ground surface in the vicinity of the pipeline. The water table has a very shallow hydraulic gradient and the aquifer's estimated hydraulic conductivity of the aquifer is 1 x 10^{-4} cm/sec.

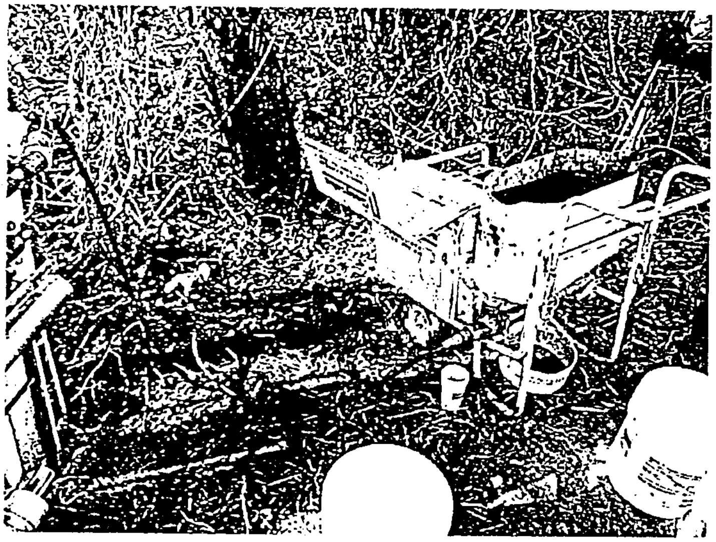
Using the laboratory analytical methodology developed by the Massachusetts Department of Environmental Protection, the groundwater contamination was determined to consist primarily of C_5 to C_8 aliphatics, C_9 to C_{12} aliphatics, and C_9 to C_{10} aromatics (Table 1). Pre-injection monitoring determined contamination levels were approximately two to three times the most conservative regulatory cleanup standard, which is applicable to drinking water sources.

A literature search indicated previous field applications of in-situ oxidation using potassium permanganate had not been overly effective at remediating C_5 to C_{12} petroleum hydrocarbons dissolved in groundwater. Nevertheless, it was selected as the remedial approach at this site for the following reasons:

(1) Site-specific considerations ruled out utilizing a hydrogen peroxide/Fenton's Reaction approach. The former jet fuel pipeline parallels a busy residential street, and both a natural gas pipeline and a water distribution main are present immediately adjacent to the former jet fuel pipeline. It was a concern that the generation of heat and gases, associated with utilizing a Fenton's Reaction approach, could detrimentally impact the adjacent pipelines and the nearby residences.

(2) Competing organic compounds, whether naturally occurring or anthropogenic, were not present. The water table was primarily fine sand with a relatively low naturally occurring organic content. In addition, contamination at the site consisted of petroleum and petroleum constituents only. Thus, there was no competing demand for the oxidant.

(3) The "inject and leave" approach for introducing potassium permanganate into the aquifer was cost effective and flexible. The ability to utilize a small geoprobe rig to inject the necessary mass of potassium permanganate into the aquifer allowed for a cost effective, low impact, and flexible remedial approach to meet the project objectives.



Potassium permanganate was introduced to the water table aquifer by injecting a solution of water and potassium permanganate via a direct push boring. Injection locations were spaced between 5 and 25 feet apart depending on the proximity to the source of the contamination with the smallest injection interval employed in the source area. A grout pump was used to force the solution into the subsurface at one or two depth intervals within the upper 5 to 10 feet of the water table aquifer. Approximately 100 gallons of solution (mixed with approximately 40 pounds of potassium permanganate) was injected at each location. The injection process, from set up on the injection location to completion of the injection quantity, required approximately 60 minutes per hole.

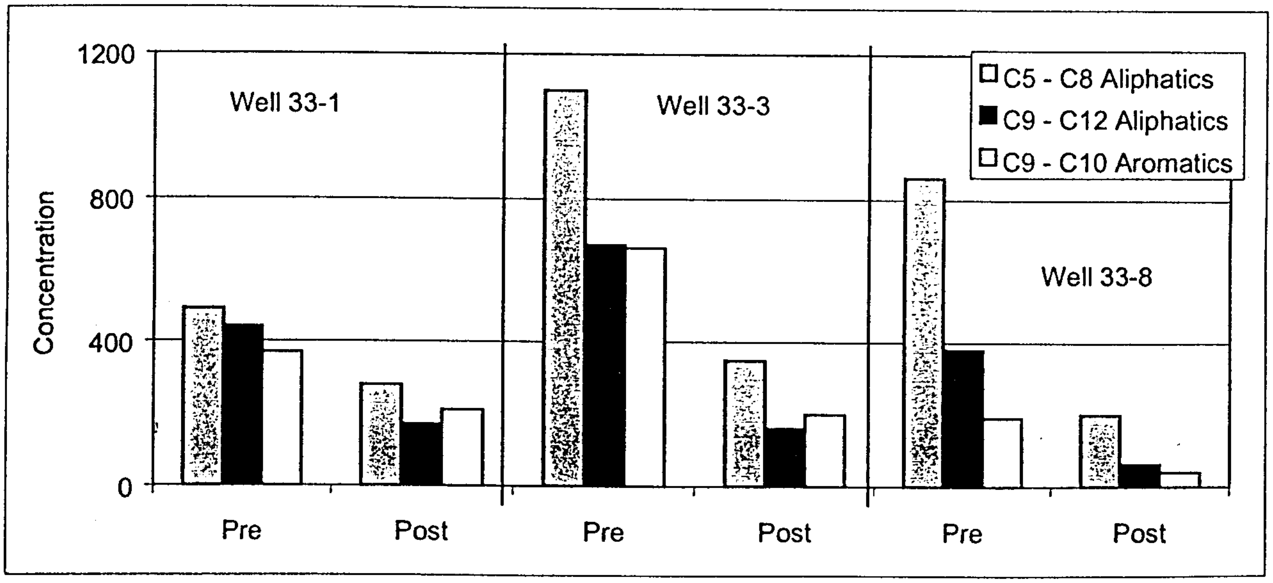
Post-injection groundwater sampling was completed approximately one week, one month, two months, and three months following the initial injection process. Results are presented in Table 1. These post-injection results show a 40% to 80% reduction in C_5 to C_{12} range petroleum hydrocarbon concentrations. The results indicate the "inject and leave" approach of introducing potassium permanganate to the aquifer was a cost effective and timely approach to reduce C_5 to C_{12} range petroleum hydrocarbon concentrations and achieve site closure.

Table 1
Groundwater Monitoring Results (ug/l) - Pre- and Post-Injection Monitoring

Well ID Pre- or Post-Injection	33-1 Pre	33-1 Post	33-3 Pre	33-3 Post	33-8 Pre	33-8 Post	Regulatory Standard
Volatile Petroleum Hydrocarbon Fractions							
C5 – C8 Aliphatics	490	280	1100	350	860	200	400
C9 - C12 Aliphatics	440	170	670	160	380	63	4,000
C9 - C10 Aromatics	370	210	660	200	190	40	200
Target Volatile Petroleum Hydrocarbon Analytes							
Benzene	ND (1)	ND (1)	ND (5)	ND (1)	3	ND (1)	5
Ethylbenzene	9	6	47	13	65	12	700
Toluene	4	ND (5)	ND (5)	ND (5)	ND (2.5)	ND (5)	1,000
m&p xylene	15	6	120	28	110	18	10,000
o-xylene	3	ND (5)	18	ND (5)	ND (2.5)	ND (5)	10,000
MTBE	ND (1)	ND (5)	ND (5)	ND (5)	ND (2.5)	ND (5)	70
Naphthalene	ND (11)	ND (5)	15	11	ND (11)	ND (5)	20

Notes: (1) Concentrations in micrograms per liter.
(2) ND = Not detected at detection limit shown in parenthesis
(3) Samples analyzed using the Massachusetts Department of Environmental Protection Volatile Petroleum Hydrocarbon Method

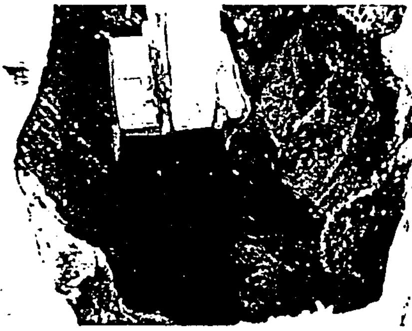
Figure 1
Groundwater Monitoring Results (ug/l) - Pre- and Post-Injection Monitoring



FORMER ELECTRONICS MANUFACTURING FACILITY, PLAINVILLE, MA
Massachusetts DEP Release Abatement Measure – Contaminant Mass Removal Activities

Key Activities:	Delineation and excavation of hot spot soils impacted with chlorinated solvents; Application of Potassium permanganate to the excavation grave to address residual contamination in soil and groundwater; Performance of field test to determine site specific oxidant demand for possible future applications of potassium permanganate.
W&C Personnel Involved:	John Thompson - project manager, regulatory negotiations Michael Doherty – senior engineer Vinutha Gowda – staff engineer

The project scope included the excavation and disposal of approximately of 30 cubic yards of soils impacted with chlorinated solvents; addition of approximately 400 pounds of potassium permanganate to the excavation grave; mixing of the potassium permanganate with the soils and groundwater in the immediate vicinity of the excavation to destroy any residual concentrations of chlorinated solvents in the subsurface soils and groundwater; and post application monitoring of downgradient groundwater quality.



The nature and distribution of constituents at the Site have been investigated since the early 1990s. Industrial chemicals identified in the environment included chlorinated hydrocarbons in soil and groundwater. During the mid 1990's, a previous consultant completed assessment and removal actions at the site and determined that natural attenuation would successfully eliminate the risk to the environment and ultimately close-out the site under MADEP regulations. However, in 1999, a MADEP audit of the site conditions found that no significant risk reduction levels had been achieved at the site. Woodard & Curran was brought in at this time to develop a closure plan that would reach a permanent solution at the site.

Woodard & Curran gained regulatory approval to perform the excavation and permanganate addition activities; developed a detailed field work plan and conducted the field activities in a timely and cost effective manner. Post application groundwater monitoring is currently on-going.

In addition, W&C also performed field test activities to determine the site specific oxidant demand of the site soils. The results from these activities will be utilized to determine the mass of potassium permanganate necessary to remediate site soils in other areas of the property if required in the future. Preliminary results from pilot test activities showed contaminated reductions in soil from 60 to 80%.

Rapid Risk-Based Site Closure Achieved Using In-Situ Chemical Oxidation

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Environmental Corporation.

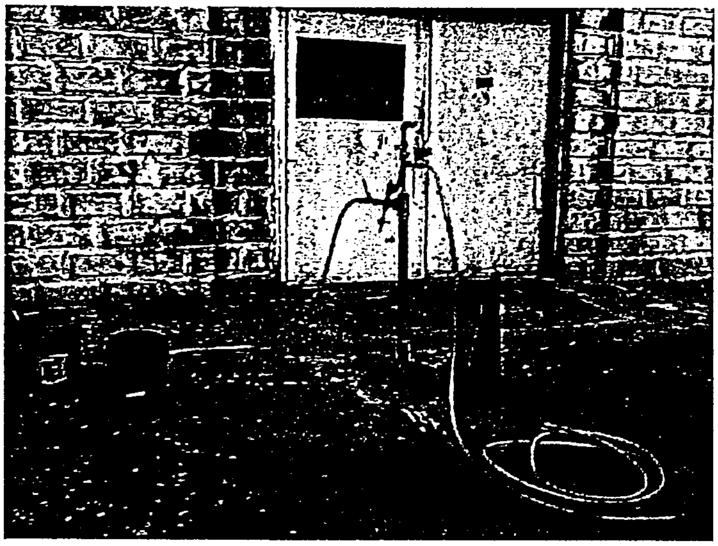
(Presented at Focus Conference on Eastern Regional Groundwater Issues, October 2000, sponsored by the National Ground Water Association and EPA Region III)

Groundwater remediation at a former industrial facility was quickly accomplished using the CleanOX® *in-situ* chemical oxidation process, a patented groundwater remediation technology which uses Fenton-like chemistry. A due diligence site assessment at the facility detected petroleum-contaminated groundwater attributable to a former #2 fuel oil underground storage tank. The former industrial facility was undergoing redevelopment by a property developer and rapid groundwater remediation was required to achieve regulatory site closure requirements and to keep the redevelopment schedule on-track. Within five months of initiating chemical oxidation remediation, the source area was remediated and contaminant levels were below risk-based closure guidelines.

Chemical Oxidation (CleanOX® Process)

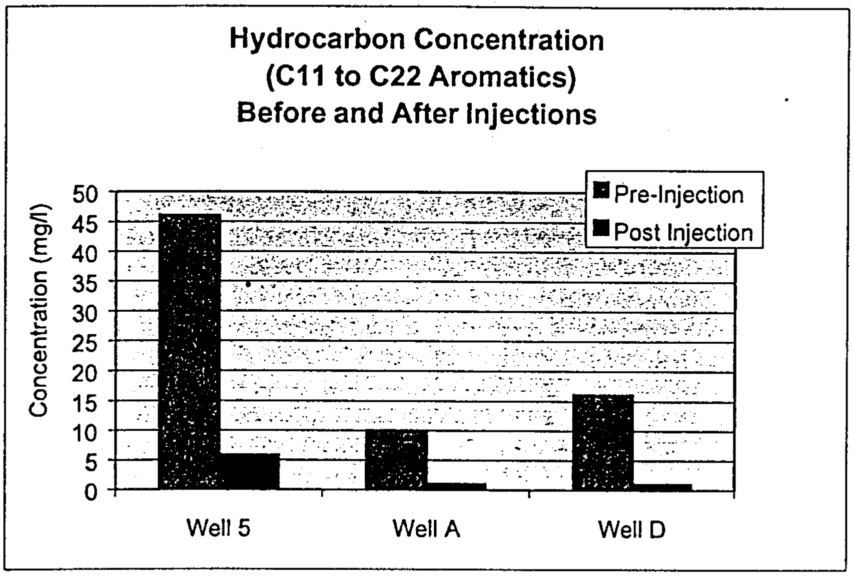
$$H_2O_2 + C_nH_x + H_2O \rightarrow 3H_2O + CO_2$$

Site assessment activities detected a 2,000-square foot petroleum plume on the property. The plume was present both adjacent to and underneath a building. Petroleum concentrations detected in groundwater samples exceeded the Massachusetts Contingency Plan (MCP) Upper Concentration Levels. Soil underlying the site consisted of fine-grained sand with lenses of silty fine sand and silt. The aquifer's hydraulic conductivity was estimated to be 3.5×10^{-5} cm/sec based on slug test results. Groundwater occurred approximately 20 feet below ground surface, although the basement of the on-site building was approximately 15 feet below grade, making the depth to groundwater under the building (where petroleum had migrated) five feet.



Prior to initiating the *in-situ* remediation, a laboratory bench test using site groundwater proved the CleanOX® process effectively degraded the site's organic contamination to carbon dioxide and water. Six two-inch diameter injection wells were installed within the groundwater plume to ensure delivery of the liquid chemical formulation to the contaminated groundwater. After lowering the aquifer's pH, hydrogen peroxide was introduced into the aquifer to oxidize the organic contaminants. Aquifer geochemistry was continually monitored throughout the injection process to ensure the stability of the chemical reaction.

After a single chemical oxidation treatment cycle, which lasted about 10 days, and a two-week stabilization period, significant reductions in petroleum concentrations were measured in groundwater samples collected from most monitoring wells. A second cycle of the CleanOX® process was implemented approximately one month following the initial injections. This second cycle focused on the former tank location where petroleum concentrations were highest. Groundwater monitoring following the second application cycle indicated that petroleum concentrations in groundwater across the entire site had decreased by more than 90%.



An MCP Risk Characterization was completed based upon the results of multiple groundwater sampling rounds and concluded the site posed No Significant Risk. Site documentation was submitted to regulatory officials to achieve site closure and to maintain unrestricted future use of the property. Site remediation and monitoring activities, which were completed while the property was undergoing redevelopment, were accomplished within a five-month period which allowed site redevelopment to maintain an aggressive schedule.

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Other Woodard & Curran Experience with In-Situ Chemical Oxidation

Manufacturing Facility, Attleboro, MA

In 2000, Woodard & Curran implemented a successful application of potassium permanganate to address site soils and groundwater that had been impacted by ammonia from an above-ground tank leak at a manufacturing facility in Attleboro, MA. After determining that the tank release had resulted in the presence of dissolved ammonia in groundwater, Woodard & Curran developed a work plan that included the excavation and disposal of approximately of 20 cubic yards of soils impacted with ammonia; addition of approximately 200 pounds of potassium permanganate to the excavation grave; mixing of the potassium permanganate with the soils and groundwater in the immediate vicinity of the excavation to destroy any residual concentrations of ammonia in the nearby subsurface soils and groundwater; and post application monitoring of down-gradient groundwater quality. As a result of these activities, ammonia concentrations in groundwater were reduced by over 80%.

In-Situ Oxidation Technology Feasibility Testing, Superfund Site, Maine

In 1997-1998, Woodard & Curran staff took the lead in developing work plans, designing the site-wide testing approach and performing the field test activities to evaluate the effectiveness of potassium permanganate as an in-situ oxidation technology to address chlorinated hydrocarbons in the soils and groundwater at the site at a superfund site in Maine. During this field test activities, over 3,500 pounds of potassium permanganate was injected into the subsurface through a series of twenty injection wells located over an acre site.

Due to the favorable results of the feasibility testing, and subsequent applications of potassium permanganate into the impacted aquifer, the client received the necessary approvals from state and federal agencies to stop operation of a costly groundwater pump and treat system that was being operated at the site. Thereby providing the client with a significant cost savings over the life of the project.

Former Electronics Facility, Cambridge, MA

In 1997, Woodard & Curran implemented a successful application of CleanOX®, a patented in-situ oxidation technology, to address dissolved chlorinated volatile organic compounds (tetrachloroethylene and trichloroethylene) in groundwater at a remediation project in Cambridge, MA. The property was formerly used to manufacture transistors, wafers, chips, and discs for the electrical components industry. During a "due diligence" assessment, chlorinated VOCs at concentrations above regulatory standards were detected in groundwater at two discrete locations on the property. The release was attributed to discharge of solvents to a leaking sewer main. A 4-inch diameter injection well was installed at each location. These injection wells were constructed with well screens extending to the top of a peat layer which occurred approximately 13 feet below ground surface. A pilot test was completed to evaluate the appropriate concentration of hydrogen peroxide to inject into the subsurface. Based on this study, a solution of 17.5 percent hydrogen peroxide was injected into the water table aquifer. A vigorous exothermic reaction was monitored during injection. After one application of hydrogen peroxide was completed, post-injection groundwater samples were collected and the dissolved levels of VOCs were found to be less than site closure goals. No additional remediation actions were needed, and a Class A-2 Response Action Outcome (RAO) Statement was submitted to the Massachusetts Department of Environmental Protection to achieve regulatory site closure. While Woodard & Curran completed this site remediation, the site was re-developed for use as office space and a glass blowing studio.

Former News Publisher Facility, Framingham, Massachusetts
(as presented in *Field Applications of In-Situ Remediation Technologies: Chemical Oxidation*, EPA 542-R-98-008, September 1998)

Woodard & Curran monitored a pilot and full-scale application of *in-situ* chemical oxidation (CleanOX®) for the remediation of 1,1-dichloroethene (DCE), 1,1,1-trichloroethane (TCA), and vinyl chloride (VC) in groundwater at a former news publisher facility in Framingham, Massachusetts, in 1996. A dry well discovered during a site assessment contained chlorinated solvents and petroleum hydrocarbons from disposal of ink and degreaser wastes. The area of cleanup consisted of crushed stone and soil surrounding the former dry well. Soil surrounding the dry well was a fine-grained silty sand. Depth to groundwater averages approximately 2½ ft below ground surface. The contaminant plume was approximately 80 x 80 feet. Pre-treatment concentrations of TCA in the two monitoring wells were measured at 40,600 and 4,800 µg/L, and VC concentrations were 440 and 110 µg/L.

A pilot -scale application was conducted to evaluate site-specific geochemistry. Two CleanOX® application points were used over a 3-day period for treatment within the 30-foot diameter dry well area. The application involved a solution of hydrogen peroxide, an iron catalyst, and an acid to control pH. Two 4-in diameter PVC wells and five surrounding monitoring wells were sampled prior to application and re-sampled 3 weeks after treatment Samples collected 3 weeks after the treatment indicated that TCA at the two contaminated wells dropped from 40,600 to 440 µg/L and from 4,800 to 2,300 µg/L. Concentrations of VC dropped to levels ranging from below detection to 85 µg/L in nearby wells.