88497

Morrison Knudsen Corporation
Federal Projects Division

WSSRA PROJECT REVIEWS AND APPROVALS

W.P. NO. 550 TASK NO. 900 DOC. NO. 3840-C: HG-K-05-4815-00

W.P. TITLE: In-Situ Chemical Oxidation of TCE in Groundwater

QUALITY LEVEL 2

LEAD DISCIPLINE Hydrogeology

SUBJECT: WSSRAP – Groundwater Operable Unit Chemical Oxidation Treatment Technologies Overview– Rev. 0 Technical Memorandum No. 3840TM-5032-00

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WELDON SPRING SITE REMEDIAL ACTION PROJECT

WSSRAP GROUNDWATER OPERABLE UNIT (GWOU)
CHEMICAL OXIDATION TREATMENT TECHNOLOGIES OVERVIEW

Task 900

Technical Memorandum No. 3840TM-5032-00

October 2000

Rev. 0

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WSSRAP
Chemical Plant
Technical Memorandum No. 3840TM-5032-00
Task No. 900
GWOU - Chemical Oxidation Treatment Technologies Overview

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1.0 INTRODUCTION

This technical memorandum is an overview of the current technology for the in situ treatment of chlorinated solvents in groundwater using chemical oxidation. The purpose of this memorandum is to provide a summary understanding of the chemical oxidation applications available for in situ groundwater treatment, and to supply technical information that is useful for the preparation of design criteria and performance specifications for the Groundwater Operable Unit (GWOU) Fenton treatment (Work Package 550) bid documents.

Many documents and internet resources were reviewed to supply information for this technical memorandum. In situ methods of groundwater treatment are being researched on a number of fronts, both in the government and private sectors. To assist government and private remediation projects, a number of governmental entities and technical groups have focused on emerging technologies for in situ groundwater remediation. Some of these groups and their respective internet sites are given below:

U.S. Department of Energy:

- Office of Science and Technology, http://www.osti.gov/
- Subsurface Contaminants Focus Area, http://www.envnet.org/scfa/
- Office of Environmental Management (EM): TechCon ("Technology Connection") Program, http://www.web.ead.anl.gov.techcon/index.cfm
- Office of Environmental Management (EM): Innovative Treatment Remediation Demonstration Program, http://www.em.doe.gov/itrd/

U.S. Department of Defense:

- Strategic Environmental Research and Development Program (SERDP), http://www.serdp.org/
- Environmental Security Technology Certification Program (ESTCP), http://www.estcp.org

U.S. Environmental Protection Agency:

- Technology Innovation Office (TIO): http://www.epa.gov/swertio1/
- (affiliated) Ground Water Remediation Technologies Center (GWRTAC): http://www.gwrtac.org/

Federal and State Cooperatives:

- Interstate Technology and Regulatory Cooperation Work Group: DNAPLs/ Chemical Oxidation Work Team, http://www.itrcweb.org/common/default.asp
- Federal Remediation Technologies Roundtable: (DOE, EPA, DOD, DOI, DOC, DOA, NASA), http://www.frtr.gov/
- Interagency DNAPL Consortium: (DOE, DOE, EPA, NASA), http://www.getf.org/dnaplguesl/

These research groups have prioritized the sharing of information with other federal agencies and the private sector. They also jointly encourage and sponsor (in the form of field demonstration sites) the use of innovative in situ technologies for groundwater cleanup.

Through its Innovative Technology Program, the Department of Energy (DOE) has completed demonstration projects using in situ chemical oxidation for the remediation of chlorinated solvents in soil and groundwater at three sites: Savannah River Site, Aiken, SC; Portsmouth Gaseous Diffusion Plant, Piketon, OH; and Kansas City Plant, Kansas City, MO (ESTCP, 1999). In addition, the Department of Defense (DOD) has utilized in situ chemical oxidation technology at a number of sites for the remediation of VOCs including chlorinated solvents. Most

applications of this technology have been performed on a pilot scale, but some have progressed to full-scale operations.

1.1 TCE Contamination at the GWOU

TCE contamination of groundwater at the chemical plant area is localized, primarily in the vicinity of the raffinate pits within two zones (DOE, 1999a). Recent TCE concentrations range from 0.5 to 870 µg/L, compared to the EPA Maximum Contaminant Limit (MCL) of 5 µg/L. The shallow aquifer beneath the chemical plant is made up of fractured, weathered limestone that is highly heterogeneous because of weathering, solutioning, fracture patterns, and paleochannel development on the bedrock surface. The paleochannels, mapped from extensive borehole data, have been correlated with troughs in the potentiometric surface of the shallow aquifer. Conduit flow in the paleochannels is indicated by dye tracer testing, which has measured average groundwater velocities of up to 2 ft/min (DOE, 1999a).

The source for the dissolved TCE in groundwater at the chemical plant has not been identified with certainty (MK Environmental, 1997); however, the presence of TCE is believed to be a relatively recent occurrence (DOE and DA, 1997). Potential source zones are waste drums removed from the southeastern corner of Raffinate Pit 4 and contaminated soils and sludge in Raffinate Pits 3 and 4. Although sampling of oil residues from the drums in Pit 4 indicated TCE at levels up to 280,000 µg/kg, samples from the underlying soils and sludge from the pits did not indicate any significant TCE source. It is possible that the source may have already been depleted (DOE and DA, 1997). The selected remedial alternative (DOE, 1999b) for the GWOU will focus on the reduction of dissolved TCE contamination in groundwater.

1.2 In Situ Chemical Oxidation Treatment

For many years, chemical oxidation processes have been widely used to treat organic contaminants in drinking water and municipal and industrial wastewaters (Siegrist, 1998). However, treatment of soils and groundwater at contaminated sites is a relatively recent application and is receiving increasing attention due to its relative ease, low cost, and speed. The cost of chemical oxidation reagents is relatively low, so their use is generally far less costly than other active source removal technologies such as in situ thermal treatment or flushing using cosolvents. Since the reaction time is near-immediate, treatment is far more rapid than biological techniques and can be faster than thermal or vapor recovery technologies (ESTCP, 1999).

In situ oxidation has only been commercially practiced for the last 5 to 6 years, and accordingly, the technology is rapidly evolving based on a better understanding of the technology's limitations and the engineering approaches to overcome those limitations (ESTCP, 1999). There are a number of chemical oxidants and a variety of methods for delivery of the oxidant to the contaminated media. Oxidants that have been typically used for remediation of soils and groundwater are:

- hydrogen peroxide (H_2O_2), including Fenton's Reagent ($H_2O_2 + Fe^{2+}$)
- permanganate (potassium, $KMnO_4$, and sodium, $NaMnO_4$)
- ozone (O_3)

Each of these treatments has been applied at pilot or full scale at government or private remediation project sites with varying success. Table 1-1 below is extracted from a recent survey of 42 sites performed by the DOD's Environmental Security Technology Certification Program (ESTCP, 1999) where in situ chemical oxidation treatments were carried out at private, DOD, and DOE sites.

Table 1-1. Characteristics of 42 sites where in situ chemical oxidation has been applied.

		DOD Sites	DOE Sites	Private Sites	Total
Number of Sites		14	3	25	42
Contaminants	CVOC[1]	6	3	10	19
	BTEX/TPH[2]	5	--	16	21
	Both	1	--	--	1
	Unknown	2	--	--	1
Media Treated	Soil Only	0	0	0	0
	Groundwater	2	0	17	19
	Both	10	3	7	20
	Unknown	2	--	1	3
Oxidant Used	Hydrogen Peroxide (Fenton)	12	1	24	37
	Potassium Permanganate	1	2	1	4
	Ozone	1	0	0	1
Vendor	GeoCleanse	8	1	4	13
	CleanOx	3	0	13	16
	ISOTEC	1	0	7	8
	Other	2	2	1	5
Scale of Treatment	Pilot/Demo Only	9	3	15	27
	Full On	1	0	4	5
	Both	4	0	6	10
Outcome	Success	5	1	11	19
	Failure	6	0	0	6
	Uncertain	3	0	14	17

[1]CVOC = Chlorinated volatile organic compounds (e.g., TCE, PCE, DCE)
[2]BTEX/TPH = Benzene, Toluene, Ethylbenzene, Xylene (volatile organic aromatics)/Total Petroleum Hydrocarbons
Outcome determinations are relative terms based on available information provided by the facility representative and denote the technology's ability or lack thereof to satisfy facility specific program performance objectives.

Pilot-scale tests were completed at all of the 14 DOD sites, with at least five tests proceeding to full scale, indicating they were successful. All but two sites were treated using hydrogen peroxide (Fenton's Reagent). Discussions with site contacts indicate that six tests were considered failures (including one subsurface explosion that terminated in situ treatment at the site). The three DOE sites were considered demonstration projects, but only one is listed as a

full-scale demonstration. Of the three DOE sites, two sites were treated with potassium permanganate and one was treated with Fenton's Reagent

All of the treatments at the 25 private sites were described as successes. Ten of the sites have proceeded to full-scale application with others to follow. The description of these treatments as successes (e.g., the state issues a No Further Action letter) is, in many cases, based on relatively little long-term data to judge the potential for rebound in groundwater concentrations. It is understood that failures are more likely to be reported at government sites than at private sites; therefore, the extent of failure is probably more prevalent than these results indicate (ESTCP, 1999).

1.3 Regulatory Issues

Application of chemical oxidants for groundwater treatment generally involves the direct injection of the oxidant into an aquifer through an injection well. Injection wells are regulated by the Underground Injection Control (UIC) program under the Federal Safe Drinking Water Act. The purpose of the UIC program is to protect underground sources of drinking water by prohibiting injections that may affect water quality. Under the UIC program, injection of any fluid into a well is prohibited, except as authorized by permit or rule. Injection of chemicals for the purpose of aquifer remediation and experimental technologies is distinguished from hazardous waste injection and is designated Class V under the UIC program. Contaminated aquifers at Superfund sites may not necessarily serve as underground sources of drinking water, and therefore, UIC requirements may not apply to wells at CERCLA sites (EPA, 1996).

Missouri is among 25 states with a UIC program that has been delegated complete primacy. In some states, variances have been granted from rules that prohibit "zones of discharge" for discharges through remediation wells. Typically, these variances are contingent upon the following (ITRC, 2000):

- A corrective action plan must be approved by the governing state agency.
- The discharge must be through an underground injection control well that meets all the applicable construction, operating, and monitoring requirements of the state agency.
- The zone of discharge must be acceptable to the state agency, typically a 10-ft radius from the point of injection but always within the contamination plume.
- The rate and volume of reagent injection must not cause undesirable migration of either the reagents or contaminants already present in the aquifer.
- The corrective action plan must address groundwater monitoring requirements associated with the use of the technology based on site-specific hydrogeology and conditions.

Missouri regulations currently prohibit injection that exceeds groundwater protection criteria. Site-specific criteria may be used only for a contaminated aquifer, and for permitted projects, all of the injectant must be removed from the aquifer (EPA, 1996).

2.0 FENTON'S REAGENT (H_2O_2 and Fe^{2+})

In the 1890s, H.R.H. Fenton developed a process that oxidized malic acid using hydrogen peroxide and iron salts. This chemistry has been and is still widely used in the wastewater industry for treating organic wastes. For this method, hydrogen peroxide is the active ingredient in oxidation of organic compounds. The hydroxyl radical is the reactive species in the process (Jerome et al., 1997).

Hydrogen peroxide is a powerful oxidant that has been used to treat wastewater for over 50 years (DOE, 1999c). Its oxidation potential is one of the highest among all oxidizers, as shown in Table 2-1.

Table 2-1. Oxidizing potential and relative oxidizing power of selected oxidants.

Oxidant	Oxidation Potential (volts)	Relative Oxidizing Power (Cl_2 =1.0)
Fluorine (F)	3.03	2.23
Hydroxyl radical (OH• from Fenton's Reagent)	2.80	2.06
Ozone (O_3)	2.07	1.52
Hydrogen Peroxide (H_2O_2)	1.78	1.31
Permanganate (MnO_4)	1.68	1.24
Chlorine Dioxide (ClO_2)	1.57	1.15
Chlorine (Cl)	1.36	1.00
Bromine (Br)	1.09	0.80
Iodine (I)	0.54	0.39

2.1 Technology Description

Fenton's chemistry (i.e., Fenton's Reagent) is essentially hydrogen peroxide (H_2O_2) combined with an iron salt (Fe^{2+}) catalyst. In the reaction, H_2O_2 is decomposed by Fe^{2+} to form highly reactive hydroxyl radicals, as expressed by the following equation (ITRC, 2000):

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

When applied to contaminated media in a low-pH environment, the hydroxyl radical (OH•) can non-selectively attack carbon-hydrogen bonds in organic compounds (Yin and Allen, 1999). The Fenton's Reagent reaction is very fast and much more efficient than using H_2O_2 alone. With chlorinated hydrocarbons such as TCE, the reaction is to degrade the compound, as represented in the following stoichiometric reaction equation (ESTCP, 1999):

$$H_2O_2 + C_2Cl_3H \rightarrow 2CO_2 + 3H^+ + 3CL^- + 2H_2O$$

hydrogen peroxide, TCE, carbon dioxide, hydrogen, chloride, water

The reaction products that are released into the subsurface are generally considered safe for the environment (ITRC, 2000). Fenton's Reagent oxidation is most effective under acidic conditions (e.g., pH 2 to 4) and becomes less effective to ineffective under moderate to strongly alkaline conditions and/or where free radical scavengers are present. The reaction is strongly exothermic and can create substantial gas, vapor, and heat (Siegrist, 1998). This has been a health and safety problem at some sites where the reaction heat volatilized organic compounds in the groundwater and vadose zone, and the VOCs migrated to the ground surface.

An important consideration in the design and application of Fenton's Reagent for groundwater remediation is the presence of carbonate soil minerals or hard water conditions in the aquifer. Carbonate minerals react vigorously with acids (commonly applied with the Fenton catalyst to lower the pH), requiring higher reagent volumes and, in many cases, precluding application in limestone environments. Dissolved carbonate in water (as bicarbonate ion) also reacts with acid and is a free radical trap reducing the efficiency of the oxidant (Bryant and Wilson, 1998).

2.2 Advantages and Limitations

Through the application of Fenton's Reagent at various sites, advantages and limiting factors specific to this chemistry have been noted. To maximize the effectiveness and minimize unwanted results from the treatment, these factors should be carefully considered when choosing this chemical oxidation method and its applicability to a site and during the design phase. The advantages and limitations of the Fenton process for in situ treatment of groundwater are listed in Table 2-2.

Table 2-2. Advantages and Limitations of Fenton's Reagent as applied to remediation of volatile organic compounds in groundwater (ITRC, 2000 and ESTCP, 1999).

Advantages	Limitations
1. H_2O_2 is abundant and relatively inexpensive.	1. Requires acidic environment for effectiveness which can be problematic in limestone aquifer.
2. Under ideal conditions it is a very efficient and strong oxidizer of organic compounds (including chlorinated solvents) without the production of toxic daughter products.	2. Hazardous intermediate compounds may be formed due to incomplete oxidation caused by • Insufficient quantity of either oxidant or catalyst. • The presence of interfering compounds (natural organic-rich media, iron and/or manganese) that consume the reagent. • Inadequate mixing or contact time between the contaminant and oxidizing agent.
3. Very fast reaction time. This leads to significant concentration reductions at source areas over a short period and reduced cost over the life of the project.	3. Very fast reaction times can limit the application's area of influence.

4. Low regulatory resistance (degrades rapidly in water with little byproducts of oxidation).	4. Creates an extremely exothermic reaction, which can boil water out of the aquifer or, as in one case, ignite generated off-gas resulting in a subsurface explosion. Off-gas and volatilization of contaminants can be an inhalation concern for personnel at the ground surface
5. More field experience in its use on pilot and full scales than any other oxidant.	5. Soil/rock containing carbonate (as in limestone), bicarbonate and/or organic matter create competing reactions that hinder effectiveness.
6. Increases dissolved oxygen (DO) levels in groundwater throughout the treatment area, which aids in bioremediation or aerobic microbial consumption of contaminants.	6. Oxidizer is unstable and extreme caution in handling is required
7. The chemistry of the process is well-known and understood and has widely been used in wastewater applications.	7. Redox-sensitive contaminants may be mobilized under oxidizing conditions
8. Since H_2O_2 degrades rapidly in the environment, excess oxidant in the subsurface does not represent an environmental impact.	8. Reagent can be scavenged by natural organic matter (NOM) in an aquifer, requiring very large application volumes.

2.3 Site Applications

In situ treatment of chlorinated solvents in groundwater using Fenton's Reagent has been performed at a number of government and private sites (see Table 1-1). In 1997, the DOE performed a pilot-scale demonstration project for groundwater remediation using Fenton oxidation at the Savannah River Site (SRS) in Aiken, South Carolina. In one area of the site, over 3.5 million pounds of solvents, primarily PCE and TCE, were discharged to the soil and groundwater between 1958 and 1985 (Bryant and Wilson, 1998). The demonstration was a cooperative venture between Westinghouse Savannah River Company and Geo-Cleanse International Inc.

The area selected for the demonstration was adjacent to the source area in a bowl-shaped depression where TCE and PCE had been discharged to the soils and groundwater. Concentrations of PCE in soil in the test area ranged from 10 to 150 mg/kg with the highest concentrations in a zone at approximately 140 ft below ground surface. Dense non-aqueous phase liquid (DNAPL) was also observed at this depth perched on a thin clay seam that is approximately 15 ft below the water table. The average concentrations of PCE and TCE in groundwater were 119.5 and 21.3 mg/L respectively, with an estimated 600 lbs of DNAPL in the treatment zone.

The performance demonstration was conducted over a 6-day period in April 1997 during which approximately 16,000 liters of 50 percent hydrogen peroxide plus catalyst solution were delivered to the aquifer consisting of interbedded and clay-rich sands (Bryant and Wilson, 1998). Four high-pressure injectors were used to deliver the solutions to the aquifer. Post-injection sampling showed a destruction of about 560 pounds of DNAPL which is a 90 percent reduction for the treatment zone (ITRC, 2000). Average groundwater concentrations of PCE were reduced

from 119.5 to 0.65 mg/L and TCE from 21.3 to 0.07 mg/L. Rebounding did occur one year after treatment but can be attributed to small DNAPL product globules not treated (DOE, 1999b).

Examples of other facilities where Fenton's Reagent has been used for in situ treatment of chlorinated solvents in groundwater, either at pilot or full scale, are provided in Table 2-3.

Table 2-3. Applications of Fenton's Reagent for remediation of chlorinated solvents in groundwater (ESTCP, 1999 and Yin and Allen, 1999).

Site Location/ Responsible Party	Project Scale and Status	Remedial Objectives	Ability to Meet Objectives/ Follow-up Actions
Kings Bay NSB, Camden County, NH/DOD	Full scale. Project is complete.	Aggressive source reduction with chemical oxidation to reduce total VOCs (primarily TCE) to 100 ppb in source area.	Able to reduce total VOCs in the primary treatment zone below 100 ppb. Success of the project may be linked to sandy soil with high K (30 ft/day). State rescinded the consent order and allowed shutdown of pump and treat system. Natural attenuation to polish residuals outside the source area
Pensacola NAS, Pensacola, FL/ DOD	Full scale. Project is complete.	To significantly reduce VOC (particularly TCE) contamination in the aquifer.	Groundwater results after Phase 2 indicate that in situ oxidation was successful in remediating chlorinated organics in the treatment zone. However, the site experienced rebound after Phase 1 and expects it again after Phase 2. State allowed pump and treat to be permanently discontinued. Monitored natural attenuation will be final alternative.
Letterkenny Army Depot, Franklin County, PA/DOD	Pilot scale. Project is complete.	Evaluate pilot test results to determine whether in situ oxidation alone or with other technologies can be used for full-scale remediation.	Not Available. This site has a fractured bedrock aquifer that has undergone active remediation for TCE and other chlorinated solvents using in situ Fenton oxidation. Results for bedrock action not available.

Costs associated with the application of hydrogen peroxide based on the stoichiometry in the equations for oxidation of TCE can be calculated. The weight ratio (lb of oxidant per lb of TCE fully oxidized) is 0.8 (ESTCP, 1999). Typical costs are approximately $1.10 per pound of hydrogen peroxide (normally sold as a 50 percent solution). Therefore, the oxidant costs per pound of TCE destroyed would be $0.88 using 50 percent peroxide. The use of peroxide would also require additions of other reagents to acidify the subsurface and/or increase the iron concentration (iron catalyst in Fenton's Reagent). In addition, inefficiencies of the peroxide caused by natural organic matter or other hydroxyl radical traps can increase the amount of peroxide needed and increase the cost per pound of TCE destroyed.

3.0 POTASSIUM PERMANGANATE

Potassium permanganate ($KMnO_4$) has been widely used in wastewater applications and to treat pollutants in drinking water for over 50 years (DOE, 1999d). In recent years, it has been used to remediate sites with soils and groundwater contaminated with organics using various techniques

for delivery of both aqueous and solid permanganate. Delivery processes that have been demonstrated include deep soil mixing, hydraulic fracturing, multi-point vertical lancing, horizontal well recirculation, and vertical well recirculation. These methods are discussed later in Section 5.

$KMnO_4$ technology is becoming popular in the remediation industry. Florida and Kansas have adopted it as a preferred technology for dry-cleaning solvent (PCE) remediation programs (Amarante, 2000). $KMnO_4$ is a dry crystalline material that turns bright purple when dissolved in water. The purple color acts as built-in indicator for unreacted chemical. Reacted $KMnO_4$ is black or brown, indicating the presence of manganese dioxide (MnO_2), a reaction by-product, which is also naturally present in soil.

3.1 Technology Description

If applied at sufficient loadings, $KMnO_4$ is an extremely effective oxidant for chlorinated solvents such as PCE, TCE, and vinyl chloride, and can be used over a broad pH range. Soil with high carbonate or bicarbonate content (as at WSSRAP) has no negative impact on its performance (Amarante, 2000). Oxidation using $KMnO_4$ involves cleavage of carbon-carbon bonds through direct electron transfer or (less frequently) by free-radical oxidation mechanisms. The stoichiometric reaction for the complete destruction of TCE is as follows (Siegrist, 1998):

$$\underset{\text{potassium permanganate}}{2KMnO_4} + \underset{\text{TCE}}{C_2HCl_3} \rightarrow \underset{\text{carbon dioxide}}{2\,CO_2} + \underset{\text{manganese dioxide}}{2MnO_2} + \underset{\text{potassium}}{2K^+} + \underset{\text{hydrogen}}{H^+} + \underset{\text{chloride}}{3Cl^-}$$

The reaction generates innocuous by-products (carbon dioxide and manganese dioxide solids) which allows for introduction of large volumes of oxidant solution. Also, there is no exothermic reaction with $KMnO_4$, making it relatively safe to apply, compared to other oxidants (e.g., H_2O_2). $KMnO_4$ is nontoxic to microbes, making it compatible with bioremediation (Amarante, 2000).

Stoichiometrically, a ratio of 2:1 oxidant to TCE is required for the chemical reaction. However, laboratory studies indicate that the reaction is optimized at a 5:1 ratio of oxidant to TCE (DOE, 1999d). Since $KMnO_4$ is insoluble in organic compounds such as TCE and PCE, the oxidation rate is dependent on the rate of solvent dissolution and mass transfer to the aqueous phase (ITRC, 2000).

3.2 Advantages and Limitations

Pilot- and full-scale testing has allowed determination of the relative advantages and limitations of $KMnO_4$ for in situ treatment of organic contaminants in groundwater. Table 3-1 details this information.

Table 3-1. Advantages and limitations of permanganate as applied to the remediation of volatile organic compounds in groundwater (Amarante, 2000, ITRC, 2000 and DOE, 1999d).

Advantages	Limitations
1. Extremely effective oxidizer of chlorinated hydrocarbons without production of toxic daughter products.	1. Potential reduction of aquifer permeability in the area of treatment from precipitation of solid MnO_2 as a reaction by-product. Also, potential increase in dissolved Mn may be regulatory concern.
2. Can be used over a wide pH range.	2. Low solubility in water.
3. Effective in an aquifer with a high carbonate or bicarbonate content.	3. Redox-sensitive metals/contaminants may potentially be mobilized under oxidizing conditions.
4. Generally no exothermic reaction with $KMnO_4$ so handling the product is relatively safe compared with other oxidants.	4. Less effective if natural oxidant demand is high and/or if abundant natural organic material (NOM) is present.
5. No off-gassing and volatilization of contaminants.	5 Unreacted $KMnO_4$'s purple color in groundwater may result in regulatory resistance.
6. Rapid reaction times and high destruction efficiencies leading to reduced remediation costs.	6. Large amounts of reagent are required for the remediation of DNAPLs.
7. Unreacted $KMnO_4$ is relatively stable in groundwater which allows: • A larger area of influence around the injection point. • Diffusion of the oxidant into media with low permeability over time further enhancing delivery to hard-to-treat contaminated zones.	7 Hazardous intermediate compounds may be formed due to incomplete oxidation caused by: • Insufficient quantity of either oxidant or catalyst. • The presence of interfering compounds (natural organic-rich media, iron and/or manganese) that consume the reagent. • Inadequate mixing or contact time between the contaminant and oxidizing agent.
8. Increases dissolved oxygen in the subsurface, which enhances bioremediation or aerobic microbial consumption of contaminants.	
9. Is easily handled, mixed, injected and controlled.	
10. Visible (purple) solution allows tracking of the injection influence or the degree of treatment.	

3.3 Site Applications

$KMnO_4$ has been applied for in situ treatment of groundwater at a number of sites (see Table 1-1). The most extensive testing of $KMnO_4$ for remediation of VOCs in groundwater has been at the DOE's Portsmouth Gaseous Diffusion Plant in Piketon, Ohio. Treatability demonstration studies of in situ chemical oxidation through recirculation (ISCOR) were performed at two locations at the facility using two variations of the process, one with horizontal wells and one with vertical wells. Both of the applications were used to treat TCE in the Gallia aquifer, a shallow silty gravel unit underlying the site that extends to a depth of about 30 ft (DOE, 1999d).

X-701B Facility: In the spring of 1997, injection and recirculation of $KMnO_4$ was demonstrated using a pair of a horizontal wells with 200 ft screened sections located within the Gallia aquifer, which is approximately 5 ft thick at this location. The horizontal wells were placed in the center of a 500 ft-wide groundwater plume emanating from a known TCE source (DOE, 1999d). Solid $KMnO_4$ was mixed with groundwater extracted from the upgradient well and re-injected into the downgradient well, approximately 90 ft away.

A solution of approximately 2 to 4 percent $KMnO_4$ was recirculated through the system for about a month. Additional injection of $KMnO_4$ was performed through a vertical well, located in the center of the treatment area, for another 8 days to enhance the delivery of the oxidant throughout the area between the horizontal wells. Results from the project showed a significant reduction in TCE, both in soil and groundwater samples. The estimated average TCE groundwater concentration in the test area was 176 mg/L before treatment, 110 mg/L at completion of treatment, and 41 mg/L 2 weeks after treatment. Of the 17 monitoring wells in the treatment zone, 13 showed a reduction from a high of 820 mg/L to ≤ 5 µg/L (Siegrist et al., 2000).

Continued monitoring indicated that the average TCE concentration for the area rebounded to 65 mg/L at 8 weeks following treatment, and 103 mg/L at 12 weeks (DOE, 1999d). These are average concentrations and are skewed high in that the treatment solution did not reach all of the monitoring wells due to heterogeneities (low permeability areas) in the aquifer. A significant finding was that for every monitoring well that showed measurable $KMnO_4$, TCE concentrations dropped to either non-detectable or low ppb levels (DOE, 1999d).

A total of 206,000 gallons of treatment solution (~12,700 kg of crystalline $KMnO_4$) was delivered to the treatment region. Treatment was discontinued in part because of a buildup of colloidal particles (MnO_2 solids) on carbon filters within the recirculation system.

5-Unit Investigative Area:
ISCOR testing was again performed at Portsmouth in 1998 using an array of vertical wells. A "5-spot" system of wells was used, where the injection well is located in the center surrounded by four extraction wells on a 45 ft radius. Again, the target zone for treatment was the Gallia aquifer, which ranged from 3 to 8 feet thick in this area. Pre-treatment concentrations of TCE in groundwater ranged from 133 µg/L to 2148 µg/L. The depth of injection was approximately 30 ft. and three pore volumes were injected over a period of 10 days using sodium permanganate ($NaMnO_4$) solution at a strength of 250 mg/L (Siegrist et al., 2000).

TCE concentrations were reduced to below the 5 µg/L maximum contaminant limit (MCL), a reduction of up to 97 percent. Oxidant was gradually depleted in 30 days, with no microbe toxicity measured and no permeability loss in the formation.

Additional examples of pilot- and full-scale projects for the remediation of chlorinated solvents in groundwater are provided in Table 3-3.

Table 3-3 Applications of potassium permanganate oxidation for remediation of chlorinated solvents in groundwater (ESTCP, 1999, and Amarante, 2000)

Site Location/ Responsible Party	Project Scale and Status	Remedial Objectives	Ability to Meet Objectives/ Follow-up Actions
Launch Complex 34 Cape Canaveral, FL/ NASA, DOE, EPA, and DOD	Pilot scale. Project ongoing.	Evaluate the complete hydrogeological, chemical and contaminant distribution changes resulting from application of $KMnO_4$ to a TCE-contaminated aquifer.	Currently in progress. Final results not available, but preliminary results for ISCOR with $KMnO_4$ show a removal efficiency greater than 99% in several monitoring wells throughout the treatment zone
BMC Olen, Irvine, CA/Private site.	Pilot Study complete, full-scale underway	Phased objectives: 1. Reduce dissolved TCE and methylene chloride to asymptote. 2. Turn off active remediation (vapor recovery and groundwater extraction. 3. Obtain site closure. 4. Achieve dissolved TVOC levels below 500 µg/L site-wide.	The treatment met the most critical goals of: 1. Reducing dissolved-phase chlorinated VOC levels (estimated at 97% reduction to low ppb levels in the injection zone). 2. Terminating active remediation by vapor recovery and groundwater extraction. The treatment did not meet the further objectives of: 1 Site closure without long-term monitoring (partly due to the unexpected presence of methylene chloride). 2 A site-wide average dissolved TCE concentration of less than 500 µg/L. Long-term monitoring will be required as part of the monitored natural attenuation strategy for residual contaminants particularly methylene chloride.

Potassium permanganate is sold as a solid for approximately $1.80 per pound. Based on the stoichiometry in the equations for oxidation by permanganate, the oxidant costs per pound of TCE destroyed would be $4.32 (ESTCP, 1999). As with peroxide, inefficiencies caused by natural oxidant demand will increase the amount of oxidant needed and will increase the cost accordingly.

4.0 OZONE (O_3)

Ozone was first used in water treatment applications more than 100 years ago (Langlais et al., 1991). With an oxidation potential of 2.07 volts, ozone is the strongest oxidant available and can quickly oxidize organic compounds once in contact (see Table 2-1). However, ozone is a gas, and therefore most suitable for treating organic contamination in the vadose zone or capillary fringe (ESTCP, 1999). Ozone has a short half-life (30 seconds in distilled water), which limits its area of influence.

4.1 Technology Description

Ozone is an allotrope of oxygen that contains three oxygen molecules (O_3), rather than the more common oxygen gas which consists of two oxygen molecules (O_2). Ozone is unstable in nature, and because of this, serves as an aggressive oxidizing agent (ITRC, 2000). Ozone can oxidize contaminants directly or through the formation of hydroxyl radicals (OH•). Contaminants oxidizable by ozone include aromatics, PAHs, pesticides aliphatic hydrocarbons (chlorinated solvents), and ordnance compounds (e.g.,explosives) (ITRC, 2000). The oxidation of TCE by ozone is represented by the following equation (Siegrist et al., 2000):

$$\underset{\text{Ozone}}{O_3} + \underset{\text{water}}{H_2O} + \underset{\text{TCE}}{C_2HCl_3} \rightarrow \underset{\text{carbon dioxide}}{2CO_2} + \underset{\text{hydrochloric acid}}{3HCl}$$

The reaction by-products are harmless in the subsurface; the HCL is buffered by carbonates in the soil or water. Ozone reacts very quickly in the subsurface and does not migrate long distances from the point of delivery (Yin and Allen, 1999).

Ozone is usually delivered to the subsurface through an air sparging system using closely spaced sparge points. Due to ozone's high reactivity, instability, and corrosivity, it is generated on site using electrical generators. In the subsurface, direct oxidation from the ozone occurs, as does oxidation from the hydroxyl radicals which rapidly attack organic contaminants (typically less than 10 seconds) and break down their carbon-carbon bonds (ITRC, 2000). For application of ozone gas in situ, there is at least one patented process of delivery, but engineered solutions using ozone are generally not proprietary. In situ application of ozone is generally delivered intermittently along with compressed air into contaminated groundwater using conventional vertical and horizontal sparging wells. Alteration of pH or the addition of a catalyst is not needed.

4.2 Advantages and Limitations

Field applications of ozone have revealed advantages and limitations of the technology for the remediation of VOCs in groundwater. These are detailed in Table 4-1.

Table 4-1. Advantages and limitations of ozone (O_3) as applied to remediation of volatile organic compounds in groundwater (ITRC, 2000 and Amarante, 2000).

Advantages	Limitations
1. Applied easily through sparging of the aquifer through wells or well points. Easily handled at the surface.	1. Ozone is unstable and requires onsite generation for application, which can be expensive.
2. Is 12 times more soluble than oxygen and is transferred into the aqueous phase more rapidly. High solubility is beneficial for achieving oxygen saturation in a contaminated aquifer (to enhance	2. Short half-life of ozone limits its ability to migrate through an aquifer over large distances, therefore, requires closely-spaced delivery points.

Advantages	Limitations
microbial biodegradation of organics).	
3. Is effective in remediating a wide variety of organic compounds, including those typically resistant to oxidation using conventional technologies	3. Susceptible to interference from free radical scavengers such as acids.
4. Effective in remediation of ordnance compounds (e.g. explosives).	4. Potential for reaction-generation of heat and gas in the subsurface.
	5. Redox-sensitive metals/contaminants may potentially be mobilized under oxidizing conditions.

4.3 Site Applications

In situ ozone injection was used to remediate chlorinated hydrocarbons at Nellis Air Force Base near Las Vegas, Nevada. Groundwater was treated during a pilot test conducted to determine the feasibility of using in situ ozone sparging to reduce TCE contamination in a 900 ft by 1,200 ft area along the flight line (ITRC, 2000). The system consisted of three sparge wells with locations based on a review of available site information and previous experience. Each sparge well consisted of a double-screened well with proprietary sparge points both within the well and at the bottom of the boring. A C-Sparge™ system was used to introduce fine bubbles of ozonated air below and into the plume of TCE-impacted groundwater. A submersible pump circulated water within the central part of the well to displace the vertically moving bubbles sideways, thereby increasing lateral dispersion and maximizing TCE destruction (ITRC, 2000).

The pilot system encountered many difficulties due to the low permeability of the soils. In addition, there were problems with the well packers and the electrical supply resulting in blowouts under system pressures and dead-heading of pumps. Results from the pilot test showed varying degrees of TCE reduction in wells and spargers, however, rebound in TCE levels was seen in four out of five wells and one out of three spargers (ITRC, 2000).

At another site, ozone was applied to remediate PCE in an aquifer beneath dry-cleaning facilities in Hutchinson, Kansas. A C-Sparge™ system was again used at the site to test remediation of the aquifer contaminated with 30 to 600 µg/L PCE. Ozone was injected at an average rate of 3 standard cubic feet per minute. Post-application monitoring indicated that 91 percent of the PCE was removed (Yin and Allen, 1999).

5.0 METHODS OF OXIDANT DELIVERY

There are a number of oxidant delivery systems that have been proposed and field-tested. Some that are more applicable for soil and vadose zone treatment can also be effective in treating soils below the water table. Techniques that have been used primarily in pilot or full-scale remediation of VOCs in soil are:

- Lance Permeation: involves using vertical lances to inject Fenton Reagent or permanganate solution into the soil.
- Soil Fracturing: involves creating horizontal fractures in the soil at various depths, which are then filled with permanganate to act as horizontal treatment zones.
- Soil Mixing: the oxidant is injected through a giant auger head to react and mix with contaminated soil. Used with either peroxide or permanganate.

Delivery systems more typically used to treat groundwater involve direct oxidant injection or injection with recirculation. Variations of these methods that have been used are:

- Injection of oxidant through newly-constructed or existing wells (more commonly permanganate due to process-specific pressure monitoring associated with peroxide injection).
- Injection of oxidant (Fenton Reagent) through proprietary vertically-oriented injectors, which involves patented modes of delivery and/or mixing of the oxidant and catalyst (e.g., Geocleanse® method).
- ISCOR, which involves injection of oxidant (peroxide or permanganate) into the groundwater through a series of injector wells and collection (recirculation) of treated groundwater in extraction wells. These well arrays can be either vertical or horizontal. The process is also known as vertical well flushing or horizontal well flushing.

6.0 OTHER CHEMICAL OXIDATION METHODS

Other lesser known methods of chemical oxidation are available for in situ groundwater treatment. Although they have not been used to a great extent, many of these methods show great promise in the destruction of organics in groundwater. Examples of these alternative methods are described below.

Sodium Permanganate

One variation of permanganate oxidation is the use of sodium permanganate ($NaMnO_4$) for remediation of organics in groundwater. It performs very similarly to $KMnO_4$ except that $NaMnO_4$ has a much higher solubility in water, which allows it to be used for in situ chemical oxidation at a much higher concentration (Armarante, 2000). This greatly reduces the time needed to oxidize a contaminated area. Additionally, $NaMnO_4$ can be used where the potassium ion cannot be tolerated, such as at facilities were potassium ions interfere with background radiation monitoring. DOE is using $NaMnO_4$ to remediate TCE at the Portsmouth Gaseous Diffusion Plant at Piketon, Ohio. Because potassium ions interfere with background radiation monitoring at this facility, $NaMnO_4$ offers an effective alternative for in situ chemical oxidation treatment.

$NaMnO_4$ is more expensive on a pound-per-pound basis. However, its increased ease of delivery and higher solubility save in labor and equipment costs, and reduce the remediation time. This makes it a cost-effective alternative (Armarante, 2000).

Chlorine Dioxide

Chlorine dioxide (ClO_2) has been used at a former electronics-manufacturing site in Missouri for TCE source destruction. In addition to the oxidation, the process interacts with soil mineral surfaces improving the partitioning of TCE from the soils and modifies groundwater redox conditions (Adams et al., 2000). The reduction in redox potential is beneficial for bacteria-mediated reductive dehalogenation of TCE.

Magnesium Peroxide

Treatment with variations of Fenton's chemistry such as magnesium peroxide have been developed to extend the reaction time of the oxidant in the aquifer. Magnesium peroxide is a solid that can be inserted in an existing well or constructed into a permeable barrier (RTN, 2000). The solid magnesium peroxide decomposes into oxygen and insoluble magnesium hydroxide. Phosphate can be added to the magnesium peroxide crystal to slow the decomposition rate and provides somewhat of a "time release" mechanism that controls the oxygen levels in the groundwater.

This controlled release eliminates the supersaturation of the groundwater with oxygen, typical of hydrogen peroxide applications, which can actually reduce oxygen availability in the treatment zone. The phosphate addition to the magnesium peroxide prevents supersaturation but may cause gas blockage and reduce the soil's permeability around the injection points (RTN, 2000). Regenesis Corporation has developed a proprietary magnesium peroxide formulation named Oxygen Release Compound (ORC®). The EPA evaluated ORC's ability to treat groundwater contaminated with hydrocarbons at three sites, and the technology has been demonstrated in 49 states (RTN, 2000).

BiOx® Treatment

The BiOx® process involves the application of modified Fenton's chemistry in a reagent that produces a controlled release of free radicals. According to the manufacturer, the controlled reaction eliminates the heat and pressure prevalent with processes that use only liquid hydrogen peroxide (Nuttall et al., 2000). In addition, the BiOx® process does not require a low pH range, reactions take place over a normal pH range of groundwater (6 to 8 standard units). Upon completion of the initial oxidation phase, BiOx® reagents continue to release molecular oxygen and nutrients for a period of time dependent on the contaminant flux and application rate.

7.0 CONCLUSIONS

The general conclusion drawn after researching the current state of in situ chemical oxidation technology is that, like most new technologies, the bugs are still being worked out, particularly with regard to the remediation of chlorinated solvents in groundwater. Because it is an in situ

technology, many pitfalls exist that are related to the natural hydrogeology, geochemistry, and contaminant properties, many of which are beyond anyone's control. These and other factors can easily short-circuit a remediation effort, particularly if steps are missed or taken improperly during the screening, selection, design, and operation of a chemical oxidation system. The following sections discuss the potential application of this technology to the GWOU, including the design and safety considerations necessary for a successful implementation of the process.

7.1 Application to the GWOU

Remediation of chlorinated solvents such as TCE within a fractured rock aquifer poses considerable difficulties with respect to both characterization and remediation (Fountain, 1998). Locating a solvent source zone in fractured rock is generally more difficult than in porous media. An example of this contrast is that in relatively homogeneous porous media, "clean" water in a well sample provides evidence that there is no residual solvent farther upgradient. Conversely, "clean" water in one well in a fractured rock unit provides information only on those fractures that are both upgradient and in hydraulic contact with the well (Fountain, 1998).

This difficulty comes into play again when attempting to remediate chlorinated solvents in groundwater with respect to both accessing the entire residual source zone and attaining hydraulic control. Many fractures are dead-ended, potentially providing traps for solvents that cannot be contacted with the treatment solution. In addition, diffusion of residual solvent resident in fractures into the rock matrix potentially produces a zone of high dissolved-phase concentration adjacent to the fractures. If the residual solvent is removed from the fractures or destroyed through treatment, the contamination will slowly diffuse back into the fractures and groundwater from the rock matrix (Pankow and Cherry, 1996).

Currently, there is little information available regarding the application of in situ chemical oxidation to treatment of fractured rock aquifers. EPA's Technology Innovative Office (TIO) operates a web site www.clu-in.org/fracrock devoted to technologies applied to groundwater remediation at fractured bedrock sites. The web site lists a number of project sites where remedial technologies for groundwater cleanup in fractured rock environments have been applied. Of the 24 sites, 7 have used some form of in situ chemical oxidation. References documenting the design, application process, and results gained at these sites were not available, although summary information and project contacts are available on the EPA web site.

7.2 Design Considerations and Process

Considerations

Many factors need to be addressed when selecting an in situ chemical oxidation technology for groundwater remediation. *The key to achieving performance goals using this method is to match the oxidant type and delivery system to the contaminants of concern and site conditions.* For in situ chemical oxidation to be successfully applied at the GWOU, inherent difficulties posed by the fractured carbonate rock aquifer and the nature of the contaminant (chlorinated solvent) must

be overcome. Subsurface characterization and the development of an accurate geological conceptual model that details the stratigraphy and preferred flow pathways (areas of greater transmissivity) are essential to implementing effective in situ oxidation treatment (ESTCP, 1999). It is critical that the hydrogeology and geochemistry of the aquifer be well-understood to:

- Select the best method of chemical oxidation.
- Optimize the design of the treatment system to effectively deliver the oxidant to the contaminant, within the constraints of the aquifer.
- Estimate the radius of influence and fate of the oxidant in the subsurface.
- Determine the potential for mobilization of contaminants.
- Determine the number of applications required to meet the cleanup goals.

Specific aquifer conditions and contaminant properties related to oxidant transport in the subsurface and projected chemical interactions that require measurement prior to design and application of an in situ chemical oxidation treatment system are detailed below (DOE, 1999c and 1999d).

- **Soil and groundwater pH:** to determine if the oxidant will be effective in the naturally occurring pH conditions or whether adjustment is required.
- **Soil and groundwater Eh:** to define background redox conditions and determine potential impacts on speciation and mobility of non-target contaminants (e.g., metals, uranium).
- **Natural oxidant demand:** to estimate the demand incurred on an injected oxidant by non-targeted species in addition to the targeted contaminant. These include total organic carbon (TOC), reduced Fe and Mn, sulfides, and organic acids. These all affect the need for excess reagent and ultimately impact remediation cost.
- **Soil and groundwater temperature:** temperature impacts reaction rates; low temperatures slow reaction rates, so higher temperatures are preferred.
- **Soil and groundwater alkalinity and ionic strength:** high carbonate alkalinity impacts free radical oxidation by scavenging the free radicals produced and limiting the oxidation efficiency. High ionic strength (e.g. abundant salts) can reduce reaction rates.
- **Depth of contamination:** affects injection design, limitations of oxidant type, and cost.
- **Presence of free-phase DNAPL:** allows targeting of source area with appropriate oxidant and increases oxidant demand.
- **Contaminant type and concentration:** affects the type and amount of oxidant to be applied.
- **Subsurface heterogeneities:** impacts (reduces) the ability for oxidants to contact and destroy organic contaminants. Also impacts transport and fate of unreacted oxidant.

Design Process

The design process and experience base for implementation of in situ chemical oxidation projects is still evolving. However, it recognized that the selection, design and implementation of in situ chemical oxidation must undergo a careful, stepped approach to cover all of the components necessary for successful application of this technology. The primary steps taken in the design process are given in order below (Siegrist, 1998).

1. Evaluate the site conditions and contaminant(s) of concern
2. Conceptual design of oxidant and delivery system
3. Laboratory bench-scale testing
4. Laboratory pilot-scale testing
5. Field full-scale pilot testing
6. Detailed design of oxidant dosing, amendments, delivery system, process monitoring, and control performance assessment

A guidance and technology overview document is currently in preparation covering the application of in situ oxidation at contaminated sites. This document provides guidance on the evaluation and design of in situ chemical oxidation with a focus on the use of potassium and sodium permanganates for remediation of contaminated sites (DOE, 1999d). The document will be titled: "Guidance for *In Situ* Chemical Oxidation at Contaminated Sites: An Overview with a Focus on Permanganate Systems" prepared for the U.S. Department of Energy. It will be available in the late fall of 2000 (Hicks, 2000) and will provide much-needed information and guidance regarding the selection, design, and operation of in situ oxidation systems.

Unwanted Results

Before applying any chemical oxidant to the aquifer beneath the chemical plant, it is important to note that a change (even locally) in the oxidation potential (Eh) within the groundwater can potentially mobilize redox-sensitive contaminants, such as uranium, which may have precipitated from groundwater onto the aquifer matrix under natural reducing conditions. Pre-application measurement of Eh in groundwater and the concentration of contaminants in the aquifer material (limestone rock) are critical steps in assessing the risk of mobilizing non-targeted contaminants through the application of oxidant chemistries.

A case study that illustrates the limitations and possible risks associated with in situ chemical oxidation was presented at the Second International Conference on the Remediation of Chlorinated and Recalcitrant Compounds (Roberts, 2000). Fenton's Reagent was used to treat a 0.25-acre "hot spot" portion of a dissolved chlorinated solvent plume at a former electroplating and manufacturing facility between April 1998 and July 1999. The solvents originated from previous cleaning and degreasing operations at the plant.

The aquifer beneath the site consists primarily of glacial till deposits with occasional sand lenses. Unconfined groundwater was found at approximately 20 to 25 ft below grade. The main contaminant of concern is TCE, which was not detected in any significant levels in the

unsaturated zone above groundwater plume, indicative of a non-source area (Roberts, 2000). TCE concentrations in groundwater ranged from 17µg/L up to 4,700 µg/L in wells located in the hot spot area. Chemical oxidation was selected for the remediation of the dissolved TCE because of the localized nature of the contamination, the proximity of the site regulatory threshold, and the need to implement an expedited and economical remedial alternative (Roberts, 2000).

Fenton's Reagent was delivered to the aquifer through 14 injectors over a 6-day period. A total of approximately 3,500 gallons of 50 percent hydrogen peroxide and 3,200 gallons of ferrous sulfate catalyst were injected. The process was monitored for delivery rate, peroxide concentrations, injection pressures, groundwater elevations, water quality measurements, and off-gas. Observations of bubbling and frothing within wells and on the ground surface were noted and used to help make adjustments in the injection program.

Results from the monitoring showed a significant drop in TCE concentrations in monitoring wells in the days immediately following the oxidant injection. However, the levels rebounded in some wells to 50 percent of the baseline measurement within 4 weeks. Five months after treatment, TCE concentrations in most of the wells had rebounded dramatically, in one well to one order of magnitude *higher* than had ever been measured in the previous 9 years. Another well was three times higher. The most recent groundwater sampling after 15 months shows that TCE levels have further increased in five monitoring wells nearest the center of the original "hot spot," the worst being 20 times higher that the historical pre-injection maximum concentration. Another finding was that the configuration of the plume had changed, and the size had approximately doubled.

The designers/operators of the system believe that the TCE concentrations rebounded because the oxidant was effective primarily in *preferential subsurface flow paths*. The highly heterogeneous soils of the site have a wide range of permeability. The injected oxidant likely moved predominantly through and reacted with TCE in higher permeability horizons (e.g. sand lenses), leaving the lower permeability zones (silts) partially treated. Following the treatment, adsorbed and dissolved TCE in the low-permeability units began diffusing back into the treated higher permeability zones, showing a remarkably uniform rate of rebound. The change in shape/enlargement of the TCE plume was attributed to exceeding the soil overburden pressures during injection and fracturing the soil, thereby opening up new or extending existing preferential flow paths.

Poor results from this injection project precluded any further applications. This project illustrates the potential impact of a heterogeneous aquifer on the treatibility of contaminants in groundwater. This phenomenon has also been observed at other sites with heterogeneous geology.

7.3 Health and Safety Considerations

When applying a chemical oxidation technology to a site, a number of safety considerations must be taken into account. Strong oxidants are corrosive and potentially explosive, so they require very careful handling by personnel applying the treatment. Heat and vapors generated by exothermic reactions in the subsurface can potentially cause fire or explosions (both subsurface and surface) and inhalation exposures for workers. The design and operation of any in situ oxidation system must take into account the hazards of the chemicals and the potential for vigorous uncontrolled reactions in the subsurface (ESTCP, 1999).

An example of the chemical oxidation application creating a health and safety problem occurred at Marine Corps Air Station Cherry Point, North Carolina. An in situ oxidation system consisting of four injectors released Fenton oxidation solution (hydrogen peroxide, ferrous sulfate catalyst, and phosphoric acid) into shallow groundwater at 9 to 13 ft below ground surface. On the second day of the demonstration project, the treatment caused pavement upheaval, underground explosions and fire (ESTCP, 1999). Unexpected levels of gasoline-range organics in the upper soil reacted with the peroxide resulting in excessive heat and off-gas buildup. The off-gas (which contained oxygen and organics) created enough pressure to buckle the pavement above. The off-gas also collected in existing voids around an abandoned sewer pipe where it ignited from the heat of the reaction, resulting in underground explosions and fire.

This chain of events led to the cancellation of the project. The site had not been adequately characterized to safely carry out the application of hydrogen peroxide. Lessons learned from this event shows that a number of items were not accounted for during the planning process which included (ESTCP, 1999):

- Significant near-surface organic contamination existed at the site. Where this occurs, a top-down treatment approach (treating the shallow surface area first) alleviates the problem.
- There was no venting and no system was in place to collect off gasses and relieve pressure and build-up of organics under the pavement.
- Abandoned piping was not identified and accounted for in the design of the system. Accurate utility surveys should be completed well in advance of field implementation.
- No system monitoring was performed in the upper soil zone to identify a potential runaway reaction event. Contingency procedures must include prioritized emergency actions to stop or slow the reaction. Also, no contingencies were included in the health and safety plan for below-ground explosions.

Another very recent incident demonstrates that even relatively stable oxidants such as sodium permanganate can cause serious injury. A worker involved in groundwater treatment at the Portsmouth Gaseous Diffusion Plant in Ohio suffered third-degree chemical burns over half of

his body when he applied an incompatible compound to a bucket containing a relatively small amount of the sodium permanganate resulting in a violent, uncontrolled reaction.

These two events should sound an alarm to those who are planning in situ chemical oxidation treatment projects. When working with reactive chemicals and potentially flammable contaminants, planning and design must take into account the potentially hazardous nature of the chemical reactions and how best to use engineering controls and emergency planning to mitigate these hazards.

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