

**IN SITU CHEMICAL OXIDATION
PILOT STUDY WORK PLAN
SAFETY-KLEEN SYSTEMS, INC. SERVICE CENTER
400 MARKET STREET
OAKLAND, CALIFORNIA
EPA ID No. CAD053044053**

SECOR Job No. 70005-009-08

3-8-99

Submitted By:
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March 8, 1999

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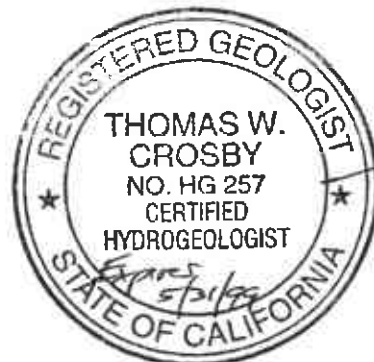
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ENVIRONMENTAL
PROTECTION

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Via Federal Express

March 8, 1999

Mr. Robert M. Senga, Unit Chief
California Environmental Protection Agency
Department of Toxic Substances Control
Southern California Region
Facility Permitting Branch
1011 N. Grandview Avenue
Glendale, California 91201

Re: *In Situ* Chemical Oxidation Work Plan
Safety-Kleen Systems, Inc., Service Center
400 Market Street
Oakland, California
EPA ID No. CAD053044053

Dear Mr. Senga:

Enclosed are three copies of the *In Situ* Chemical Oxidation Work Plan which details the activities which will be performed to evaluate the feasibility of using chemical oxidation to remediate residual VOC-impacts in groundwater at the above-referenced facility. Safety-Kleen is proposing to perform this pilot study under the existing voluntary interim remedial activities being conducted at the site. Safety-Kleen Systems, Inc. (Safety-Kleen) will implement the Work Plan within one month of receiving approval from the RWQCB and/or Alameda County.

If you have any questions, please call me at (505) 888-3952.

Sincerely,

Sara C. Brothers, CPG
Senior Project Manager - Remediation
Safety-Kleen Systems, Inc.
2720 Girard NE
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Enclosure

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Greg Hoehn, SECOR International Incorporated

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March 8, 1999
SECOR Job No. 70005-009-08

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1.0 INTRODUCTION

SECOR International Incorporated (SECOR) has prepared this *In Situ* Chemical Oxidation Pilot Study Work Plan (Work Plan) on behalf of Safety-Kleen Systems, Inc. (Safety-Kleen) to perform a pilot study to evaluate the feasibility of *in situ* chemical oxidation to remediate residual dissolved groundwater impacts at the Safety-Kleen facility located at 400 Market Street in Oakland, California (Figure 1). This Work Plan details the work scope Safety-Kleen proposes to employ potassium permanganate as the chemical oxidant for the pilot study.

2.0 BACKGROUND

2.1 Site Use History

The Safety-Kleen Oakland facility is located in a commercial and light industrial zoned area of Oakland. The facility contains an approximately 8,900 square foot office and warehouse building, two double-walled 12,000-gallon underground storage tanks (USTs), and a return and fill shelter. The tanks and return and fill shelter are located outside, on the east side of the site, between the Safety-Kleen office/warehouse building and a neighboring business (Figure 2).

Safety-Kleen started operations at the facility on February 1, 1975. The facility is a branch of Safety-Kleen's chemical distribution chain. Most of its customers are small quantity generators engaged in the auto repair and industrial maintenance business. Used chemicals including spent mineral spirits, spent immersion cleaners, dry cleaning wastes, and spent antifreeze are collected from customers and stored at the facility while awaiting shipment to recycling centers. These used chemicals are potentially hazardous waste due to their toxic and/or ignitable characteristics.

2.2 Investigation Background

In May 1986, a preliminary site assessment was conducted. The scope-of-work included the advancement of three 8-inch diameter by 20-foot deep soil borings. Two of the borings were converted to 2-inch diameter groundwater monitoring wells designated as SK-1 and SK-3 (Figure 2). The soil boring which was not converted to a well was designated as SB-1 as shown on Figure 2. Soil samples collected from each of the borings detected the presence of total petroleum hydrocarbons as mineral spirits (TPHms). Separate-phase product was noted on the water table in both monitoring wells SK-1 and SK-3 [CWC-HDR Consulting Engineers (CWC-HDR), 1986].

In June 1988, a soil-gas survey was conducted to preliminarily delineate the areal extent of subsurface impact and to assist in the placement of groundwater monitoring wells. Thirteen soil-gas probe holes were located on and around the site to a depth of 6 to 10 feet below ground surface (bgs). Vapor samples were extracted from all the probe holes and analyzed for TPHms. The resultant mineral spirits vapor plume was determined to be restricted to the parking lot and loading dock areas at the site, and was inferred to extend beneath both adjacent buildings and to the lot located to the north of the return and fill shelter (Groundwater Technology, Inc. [GTI], 1988). Seven soil samples were extracted from the capillary fringe from peripheral probe holes to verify the results of the soil-gas survey. Analyses of soil samples for volatile organic compounds (VOCs) detected VOCs slightly above the method detection limit in each of the samples; tetrachloroethene (PCE) was the predominant compound detected. No TPHms-impact was detected in the peripheral soil samples (GTI, 1988).

Nine monitoring wells (MW-1 through MW-9) were installed on and around the site from July 25 through July 29, 1995 (Figure 2). Thirty-two soil samples from these borings were analyzed for TPHms and VOCs. A total of seven soil samples had TPHms detected and five soil samples had VOCs detected above the laboratory reporting limit. VOCs were detected in soil in the borings for monitoring wells MW-3, MW-7, and MW-9. The VOCs detected in soil included methylene chloride, PCE, 1,1,1-trichloroethane (TCA), trans-1,2-dichloroethene (DCE), and chlorobenzene (GTI, 1988). Groundwater samples were collected from seven of the monitoring wells. Wells SK-1, SK-3, MW-7, and MW-9 were not sampled due to the presence of separate-phase product. No TPHms was detected in the wells sampled; however, VOCs were detected in each of the wells sampled. VOCs detected included methylene chloride, trichloroethene (TCE), 1,1-dichloroethane (DCA), 1,2-DCA, trans-1,2-DCE, chloroform, and chlorobenzene. The groundwater results indicated that a VOC plume with relatively high TCE concentrations was encroaching on to the Safety-Kleen property from the north (upgradient). Due to the presence of the encroaching plume, Safety-Kleen determined it was not feasible to initiate a groundwater pumping program without accelerating the TCE plume until a responsible party was identified and had taken responsibility for controlling the plume (GTI, 1988). A detailed description of the 1988 assessment activities is presented in the report entitled Interim Update Report, Safety-Kleen Facility, 404 Market Street, Oakland, California dated September 9, 1988.

~~Four additional monitoring wells were installed on and around the site from August 18 through September 12, 1989.~~ Monitoring wells MW-10, MW-11, and MW-12 were installed to assess the periphery of the VOC plume, and monitoring well MW-13 was installed with a discrete screen interval at the base of the uppermost aquifer to assess the vertical extent of the dissolved VOC plume. No VOCs or TPHms were detected in the eight soil samples collected for analysis from the drilling for the four additional monitoring wells (GTI, June 1990). A detailed description of the August and September 1989 assessment activities is presented in the June 1990 Update Report, Additional Assessment, 404 Market Street, Oakland, California.

Groundwater impacts have been monitored through quarterly groundwater sampling since 1988. In a letter to the DTSC dated October 8, 1998, Safety-Kleen requested the groundwater sampling be changed from quarterly to semi-annual. The change was approved by Alameda County Environmental Health Services in a letter dated November 17, 1998, with the exception that monitoring well MW-9 continue to be sampled quarterly. As requested by Alameda County, Safety-Kleen will sample monitoring well MW-9 quarterly as long as no sheen or measurable product is present in the well. The results from the October 12, 1998, sampling event are depicted on Figure 4.

2.3 Geologic and Hydrogeologic Conditions

The Safety-Kleen facility is located in the eastern San Francisco Bay area, on the East Bay Plain, between two mountain blocks of the Central Coast Range. The Berkeley Hills (East Bay Hills), a branch of the Diablo Range, lie to the east. The San Francisco Peninsula, the northernmost extension of the Santa Cruz Mountains, lies to the west. The San Andreas fault zone is west of San Francisco Bay while the Hayward

and Calaveras fault zones are to the east (Graef et al., 1990). The land surface at the facility is approximately 9 feet above mean sea level (amsl). The land occupied by the Safety-Kleen facility is essentially a flat plane which slopes slightly to the southeast. The maximum difference in elevation across the site is approximately 1.5 feet.

The Safety-Kleen facility is located approximately 6,200 feet west of Lake Merritt and 2,200 feet north of the Oakland Inner Harbor Channel which is connected to San Francisco Bay (Figure 1). There are no other surface water bodies nearby. Drainage from the active portion of the facility is discharged through a storm drain located in the driveway entrance from Fourth Street (Figure 2). The storm drain system discharges directly to the Oakland Inner Harbor Channel. The Flood Insurance Rate Map, Panel 15 of 45, indicates that the Safety-Kleen facility is outside of the 100-year flood plain (California Environmental Protection Agency [Cal-EPA], 1990).

2.3.1 Regional Geology

The geologic formations underlying San Francisco Bay are divided into two distinct units that differ greatly in age and rock type. The bedrock underlying most of the San Francisco Bay is composed of Jurassic and Cretaceous sandstone, siltstone, chert, melange, and ultramafic rocks of the Franciscan Complex. Total thickness of the Franciscan Complex is unknown. Beneath the site, Pleistocene age continental and marine sediments of the Alameda Formation (older alluvium) unconformably overlay the Franciscan bedrock and are composed of gravel, sand, silt, and clay which is locally organic rich and fossiliferous. Consolidation of the sediments increases with depth with the maximum known thickness of approximately 1,500 feet (Cal-EPA, 1990).

The Pleistocene-Quaternary Age Merritt Sand overlies the Alameda Formation (older alluvium) and consists of fine-grained sand and firm, clayey sand that contains lenses of sandy clay and clay. One to two feet of loose, sandy silts covers the surface of the sand. These sediments were deposited by wind and water from beach and near-shore deposits. Maximum known thickness of the Merritt Sand is approximately 65 feet (Cal-EPA, 1990).

No known active faults (displacement in the Holocene Epoch) are located within 3,000 feet. The Hayward fault, the nearest fault having displacement during the Holocene Epoch, is over four miles from the Safety-Kleen facility. The site is not located within an Alquist-Priolo special studies zone (Graef et al., 1990).

2.3.2 Site Geology

The subsurface geology as observed in the borings drilled in and around the site show the Merritt Sand are present beneath the site. The Merritt Sand beneath the site consist of interbedded sandy silt and sandy clayey silt (GTI, June 1990).

2.3.3 Regional Hydrogeology

The older alluvium is the major groundwater reservoir along the East Bay Plain. In the Oakland area, the older alluvium has not been subdivided into aquifer units like it has been in San Lorenzo and further south along the East Bay Plain. Groundwater in the older alluvium is present under confined conditions in a series of permeable sand and gravel beds separated by low permeability clay and silt aquitards. Recharge to the aquifers in the older alluvium occurs principally as seepage from streams along the west side of the Hayward fault. The overall movement of groundwater in the older alluvium is westward toward San Francisco Bay, but locally the movement may be altered by pumping from wells. Some upward movement of groundwater from the confined aquifers toward the overlying sediment also occurs under natural conditions. The vertical flow direction has now reversed due to pumping over the past 60 years (Graef et al., 1990).

2.3.4 Site Hydrogeology

In the Oakland area, the permeable Merritt Sand is considered only a secondary source of groundwater due to its limited areal extent and thickness. The unconfined Merritt Sand aquifer is recharged in areas of surface exposure by precipitation, seepage from streams, lawn and garden watering, excessive irrigation water, and leaky sewers (Graef et al., 1990).

Groundwater in the monitoring wells at the site and surrounding area intercept groundwater at approximately 8 feet bgs. Seasonal fluctuations can cause the depth-to-groundwater to fluctuate from approximately 7 to 13 feet bgs. A southerly groundwater flow direction has consistently been calculated beneath the site (GTI, June 1990).

2.4 Extent of Impacts to Groundwater

Based on the previous investigation events, the possible sources of contamination at the facility include the former USTs, former return and fill shelter, and unknown upgradient source(s). The UST and shelter units were replaced in 1990, greatly reducing the likelihood for additional sources of subsurface impact. The new USTs and return and fill shelter were located in the same locations as the previous units. A VOC plume has migrated from upgradient (north) of the site.

Mineral spirits and associated VOC impacts appear to have impacted the shallow soil in the vicinity of the USTs and return and fill shelter. Additionally, impacts have either directly impacted groundwater from the former USTs or have migrated from the vadose zone to the groundwater. Separate-phase product on the groundwater appears to be relatively static in the vicinity of the USTs and is present only in monitoring well MW-9 and extraction well RW-1 (Figure 2). Dissolved VOC impacts from the Safety-Kleen facility are present in monitoring well MW-8, located in the entrance on Fourth Street. VOC impacts have been present in monitoring wells MW-3 and MW-12, located downgradient from the Safety-Kleen facility;

however, these impacts may be associated with the upgradient VOC plume. A map depicting the chemical distribution in groundwater, based on the October 12, 1998 sampling event, is included as Figure 4.

The extent of contamination at the facility is well defined. Soil samples collected in 1990 during the UST replacement and during the drilling of soil borings for monitoring well installations found the soil impact is present immediately adjacent to the UST pit and has migrated along the capillary fringe as far as monitoring well MW-8. Groundwater impacts related to past Safety-Kleen operations appear to extend to monitoring well MW-8 with peripheral impacts present due to migration of an upgradient VOC plume across the site monitoring system.

2.5 Historical Remedial Efforts

2.5.1 UST Replacement

From May 31 through July 5, 1990, the three single-walled USTs (two 6,000-gallon and one 10,000-gallon) were removed and replaced with two 12,000-gallon double-walled USTs. During the removal, the tank excavation was completed to approximately 13 feet bgs. Groundwater was encountered at approximately 8 feet bgs, requiring dewatering during the installation of the new USTs. Groundwater and product that accumulated in the excavation were pumped into storage tanks pending removal of the product using a skimmer. Approximately 100 gallons of product were removed and sent to a Safety-Kleen Recycle Center. Approximately 34,000 gallons of water were treated and discharged in accordance with an East Bay Municipal District (EBMUD) permit (GTI, September 1990).

Eight soil samples were collected from the sidewalls and bottom of the tank excavation during UST replacement. The eight samples yielded detectable concentrations of TPHms. A detailed description of the analytical results is presented in the Report of Underground Storage Tank Replacement Activities At The Safety-Kleen Oakland Service Center, Oakland, California dated September 1990. Excavated soil totaling 984 tons were transported to Port Costa Materials, Inc. in Port Costa, California for thermal destruction of volatile hydrocarbons in a rotary kiln (GTI, September 1990).

Subsequent to excavation of the tank pit, two new 12,000-gallon double-walled Glasteel™ USTs were installed. In conjunction with the UST installation, soil vapor extraction (SVE) system piping and a product recovery well were installed in the excavation. The SVE system piping and recovery well were installed in accordance with the Work Plan For Soil-Vent System Piping dated June 15, 1990. Figure 3 presents the location of the recovery well and soil-vent system layout in schematic. After completion of the UST installations and SVE system and recovery well installations, the excavation was backfilled and resurfaced with concrete.

2.5.2 Soil Vapor Extraction Pilot Test

A soil-vent pilot test was conducted on January 18, 1990, to evaluate the applicability of using soil venting as a soil remediation technique. The results of the test indicated that vertical venting point could achieve a horizontal radius of influence of approximately 35 feet. The test also indicated that mineral spirits vapors could be withdrawn from the vadose zone using standard vacuum-extraction techniques (GTI, June 1990). A detailed description of the soil-vent feasibility test is included in Appendix E of the June 1990 Update Report, Additional Assessment, 404 Market Street, Oakland, California.

2.5.3 Soil Vapor Extraction System Operation

In June 1993, the SVE system operation was initiated. The SVE system consists of the seven horizontal vapor extraction lines and a vapor treatment system. Initially, the vapor abatement system consisted of a Padre™ regenerative polymer adsorption system followed by a carbon polish. A detailed description of the SVE system is provided in the Quarterly Progress Report dated December 23, 1998.

The SVE system currently consists of two 1,500-pound granulated active carbon (GAC) vessels connected in series to a manifold attached to seven horizontal vapor extraction perforated pipelines (see Figure 3). The SVE system has operated intermittently since June 1993. During operation, SVE system influent and effluent vapor samples are collected and vapor samples are analyzed for TPHms; benzene, toluene, ethylbenzene and xylenes (BTEX); and VOCs. Data collected from initial start-up through November 11, 1998, indicate a total of approximately 5,400 pounds of mineral spirits have been removed from the subsurface by the SVE system. During the implementation of the *in situ* chemical oxidation pilot study, the SVE system operation will be discontinued.

2.5.4 Product Pumping System

A product pumping system was installed in recovery well RW-1 to remove separate-phase product from the water table and began operation on January 19, 1993. The mineral spirits recovery pump that was located in recovery well RW-1 failed and was replaced by a passive recovery skimmer in November 1995. A passive recovery skimmer was also placed in monitoring well MW-9 (see Figure 2) at that time. On August 5, 1998, the passive recovery skimmer was removed and oxygen releasing compound was suspended in recovery well RW-1 in an effort to enhance site remediation by oxidizing residual impacts in the vicinity of the USTs. Mineral spirits recovered

from monitoring well MW-9 are emptied directly to the waste mineral spirits UST at the site and are incorporated into the Safety-Kleen recycling process. The amount of recovered product is recorded each time the skimmer is emptied. Measurable product has not been present in the skimmers since July 1996.

Mineral spirits product has been collected in monitoring well MW-9 and recovery well RW-1 via passive recovery skimmers and by hand bailing at the time of groundwater monitoring and sampling. The skimmer in recovery well RW-1 has been removed to facilitate the installation of oxygen releasing compound (ORC) in the well. The last measurable product recovered was in July 1996. The total volume of mineral spirits product removed from the subsurface to date is approximately 444 gallons. During performance of the pilot study, the ORC will be removed from well RW-1.

3.0 PERMANGANATE TREATMENT

Potassium permanganate (KmnO_4) is a strong oxidant that reacts well with a variety of double-bonded chlorinated hydrocarbons such as DCE, TCE, and PCE. The compound is deep purple in color, highly soluble in water (up to 10 percent by mass), and can move through aquifer sediment with little retardation. It also reacts well at high pH and persists longer than most comparable chemical oxidants such as Fenton's reagent (hydrogen peroxide, ferrous sulfate, and acid to optimize reaction conditions). The slower rate of reaction of potassium permanganate means that it does not generate excess gases which can reduce the permeability of aquifers by clogging them. In addition, permanganate's deep purple color, even in dilute concentrations, is visible with the naked eye. This facilitates monitoring of dosing in downgradient wells.

Because potassium permanganate is a more stable compound than oxidants such as hydrogen peroxide, it will remain longer in a contaminated aquifer, increasing the effectiveness of each dosing. Literature information on the use of potassium permanganate as an oxidant of VOCs is included in Appendix A. An example of the chemical reaction potassium permanganate generates in an aquifer contaminated with TCE is written below:



Potassium permanganate reactions can generate acidity, therefore, an aquifer with high alkalinity is ideal for permanganate reactions. Potassium permanganate, because it reacts slowly, can be dosed in a single concentrated slug which then gradually permeates and remediates the contaminated aquifer over time. The treatment plume will then saturate the aquifer and permeate even highly impermeable zones. The result is complete control of VOC concentrations at their sources in sediments, and accelerated destruction of VOCs directly as they desorb.

Injection of potassium permanganate within the aquifer saturates contaminated sediments with oxidant solutions. As the VOCs desorb or dissolve because of decreasing VOC concentrations in the waters surrounding the sediments, they immediately degrade to carbon dioxide and chloride. Potassium permanganate maintains a large concentration gradient surrounding highly contaminated particles as a result which increases the rate of desorption and therefore reaction and removal.

Permanganate reacts with VOCs and reduced materials in soils producing manganese dioxide, a common soil mineral. The slow water movement at the Oakland facility will minimize potential off-site impacts during the pilot test.

4.0 OBJECTIVES

The objective of the proposed pilot study is to evaluate the applicability and effectiveness of using KMnO_4 (permanganate) to permeate and treat VOC-impacted groundwater zones and destroy chlorinated hydrocarbons *in situ*. The proposed treatment is a passive remediation technology which uses ambient water flow to transport and disperse the chemical oxidant. Data collected from the pilot study will be used to assess the technology for potential full-scale implementation and provide a basis for design of a full-scale, passive *in situ* chemical oxidation system, if feasible.

5.0 SCOPE-OF-WORK

The scope-of-work for this project includes four main tasks: 1) Baseline Monitoring of Geochemical Parameters; 2) Permanganate Injection; 3) Monitoring of Degradation; and 4) Data Evaluation and Report Preparation. Upon obtaining regulatory approval for the activities outlined in this Work Plan, Safety-Kleen will initiate the pilot study. **During the performance of the pilot study, the SVE system will not be operated and the ORC will be removed from well RW-1.** Timing for completion of the outlined tasks will depend on regulatory approval and rates of chemical transformation in the field. The following subsections outline the specific tasks required for effective implementation of potassium permanganate as an *in situ* chemical oxidation treatment.

5.1 Baseline Monitoring of Geochemical Parameters

In order to assess the ambient concentration of pilot test monitoring parameters at the site, background monitoring will be conducted prior to injection of permanganate. **The injection point (RW-1) and wells downgradient of the injection point (MW-9, MW-8, MW-13, and MW-2) will be sampled for oxidation reduction potential (ORP), dissolved oxygen (DO), pH, electrical conductivity (EC), chloride (Cl), manganese (Mn), TPHms, and VOC concentrations.** These data will represent site geochemical conditions prior to permanganate injection, and will be the basis for comparison to determine the effectiveness of chemical oxidation at the site.

5.2 Permanganate Injection

Potassium permanganate solution will be injected into the central area of the Oakland site at extraction well RW-1 (see Figure 2). Well RW-1 is constructed within the fill material around the USTs. Monitoring well MW-9 is located downgradient of RW-1 and is within the area where hydrocarbon and chlorinated solvent impact has been observed. Both wells MW-9 and RW-1 are located downgradient of the off-site source for TCE and *cis*-1,2-DCE which enters the site from the northeast. **Injection into RW-1 will be monitored in downgradient monitoring wells MW-9 and MW-8, as well as off-site monitoring wells MW-2 and MW-13.**

Permanganate injection can be broken out into the separate tasks associated with the injection process: 1) permanganate solution preparation; 2) injection of the permanganate solution; and 3) monitoring during and immediately after injection.

5.2.1 Permanganate Solution Preparation

Potassium permanganate solution will be prepared by mixing the powdered reagent into clean water at a solid:solution ratio of 1:20. The permanganate powder will be mixed with water in a 600-gallon tank. Precautions will be taken to minimize dust generation during mixing and field

personnel will use protective equipment outlined in the Amendment to the Health and Safety Plan for the Permanganate Treatment Pilot Test.

Powder will first be added to the bottom of the 600-gallon tank containing a small amount of water. The powder will be scooped from the container and deposited in a manner such that little dust is generated. The water in the bottom of the tank is used to prevent dust generation during pouring. Once the required mass is added to the container, additional water will be added to fully dissolve the permanganate. A submersible pump will be used to recirculate water within the tank to ensure efficient mixing and complete dissolution of the permanganate. Care will be taken to ensure that all the oxidant is dissolved prior to injection in order that the required dose is added and solid permanganate is not injected into the well.

The volume of permanganate solution prepared is based on a desired dosing level of approximately 0.1 grams per liter (g/L) of groundwater treated for an assumed treatment zone radius around the injection well of 50 feet and an assumed impacted aquifer thickness of 20 feet. The predicted 50-foot radius of influence would account for the elliptical shape of the permanganate plume as it moves downgradient. Based on a radius of influence of 50 feet and an assumed soil porosity of 20 percent (0.2), the estimated volume of water within the treatment zone would be approximately 31,415 cubic feet or 234,990 gallons. To dose the groundwater to a concentration of 0.1 g/L (or 0.379 grams per gallon), 89 kilograms of permanganate will need to be added to the injection well. This represents approximately 470 gallons of a 5 percent permanganate solution.

One 470-gallon batch of 5 percent potassium permanganate solution will be prepared for injection into well RW-1.

5.2.2 Injection of Permanganate

Potassium permanganate will be injected into well RW-1 by using a peristaltic pump to drain the solution into the well. No external pressure in addition to the height of the water column generated by drainage of the solution into the well will be applied. Flow from well RW-1 is assumed to occur rapidly due to the relatively coarse backfill around the USTs. During injection, a tremie pipe will be used which will be placed midway between the top and bottom of the saturated screened interval. The purpose of the tremie pipe is to ensure efficient mixing of the permanganate solution throughout the water column during injection. Well RW-1 will be treated with permanganate solution at approximately 0.5 gallons per minute (gpm) or a sustainable injection rate using polypropylene tubing. The solution will be drained from just above the tank bottom using a peristaltic pump in order to prevent the direct injection of undissolved potassium permanganate into the well. Careful monitoring will be maintained during drainage to ensure that permanganate does not overflow from the well during injection.

5.2.2.1 Injection Monitoring

Breakthrough of the permanganate solution in monitoring well MW-9 will be determined through periodic sampling conducted during the injection. Presence of permanganate will be determined visually using the bright purple color of the reagent as an indicator. The approximate concentration of permanganate will be determined using an ultra-violet-visible light spectrophotometer. It is unclear how long breakthrough is anticipated to require given the heterogeneous nature of the sediments in this area. Injection and downgradient wells will be monitored monthly after injection. Low-level hydrocarbon contamination may result in higher required dosing levels, and therefore repeated dosings will most likely be required following this pilot study. Short-term duration of permanganate will be used as an indicator of residual hydrocarbon concentrations and full-scale dosing will be adjusted appropriately.

5.3 Monitoring of Degradation

Monitoring will be conducted on a monthly basis beginning one month after reagent injection. Wells will be sampled for VOCs, TPHms, ORP, DO, pH, EC, Cl, and Mn. Mn will be monitored either visually as permanganate at high permanganate concentrations, or by laboratory analysis at low concentrations when permanganate has dissipated. Visibly purple samples should not contain quantifiable concentrations of VOCs. However, VOC concentrations will be initially measured and compared to permanganate concentrations in order to determine whether VOCs are present in purple colored samples. Once it has been demonstrated that VOCs are not present in purple colored samples, purple colored samples will not be analyzed for VOCs. Once the purple permanganate color dissipates, samples will be analyzed for Mn to determine the low-level residual concentrations remaining. VOC, TPHms, Cl, and Mn concentrations will be performed by the Safety-Kleen analytical laboratory. Permanganate concentrations will be measured in the SECOR Geochemistry laboratory using an ultra-violet-visible light spectrophotometer. The other parameters (ORP, DO, pH, and EC) will be measured using field monitoring equipment.

Sampling will be conducted using submersible pumps employing low-flow purge techniques. The purge water will be stored on-site in drums pending removal by Safety-Kleen. The purge water generated after the first monitoring event will be sampled for water characterization profiling to determine if the water must be disposed of or can be incorporated in the Safety-Kleen recycling process.

6.0 QUALITY ASSURANCE PROCEDURES

A groundwater sampling and analysis plan has been developed for the site. All procedures will be conducted following these procedures to ensure that sampling is conducted appropriately and reliably. Water monitoring will be conducted in accordance to the plan developed for the site with the addition of the field test methods proposed in this Work Plan.

In addition to chloride, ORP, pH and DO will be measured using ISE's. These represent the most effective methods for analysis in the field. Quality of data will be ensured through careful field calibration using ISE meter and electrode manufacturer's recommended methods and solutions.

Laboratory analyses will be overseen by EPA-certified technicians and will be certified using EPA-certified standards and procedures. The laboratory methods followed for this pilot test include EPA Method 8260 for VOCs, EPA Method 8015 (modified) for TPHms, EPA Method 300.0 for chloride, and EPA Methods 200.7 or 6010 for Mn.

All data will be reviewed by SECOR personnel for consistency and potential laboratory or field errors. Where appropriate, statistical and geochemical modeling tools will be used to determine if data are consistent and reliable.

7.0 SCHEDULE

Permanganate injection will proceed within one month of regulatory approval of the Work Plan. Injection will require two to three work days for completion. Monitoring will be conducted for approximately six months after injection until permanganate concentrations diminish and VOC response is observed. A pilot study report (Section 8.0) will be prepared and submitted for approval within two months of receipt of the final laboratory analytical results.

8.0 PILOT STUDY REPORT

8.1 Data Evaluation and Report Preparation

The monitoring data will be compiled for comparison with initial baseline data collected prior to chemical dosing. The data will be evaluated for trends with time and distance from the injection point. The main objective of this pilot test is to determine the appropriate dose required for full-scale treatment, should permanganate be found to be effective at remediating VOCs at the site. Therefore, the data evaluation and report will focus on the feasibility of full-scale implementation, the expected duration of treatment, and the appropriate dosing concentration determined during the test. VOC concentrations will be plotted against time and different water quality parameters to determine if correlations between VOCs and field measured parameters can be used to assess the need for redosing in order to minimize the number of laboratory analyses required. The full report will include:

- Description of the chemical mixing and injection procedures.
- Description of the frequency and parameters measured during monitoring.
- Compilation of field and analytical results.
- Evaluation of field and analytical results.
- Correlation calculations with respect to dosing assessments.
- Review of the field procedures used and their reliability and usefulness during full-scale implementation.
- Evaluation of the effectiveness of the treatment in degrading specific compounds.
- Evaluation of the cost-effectiveness of the treatment.
- Estimation of the cost, number of injection points, expected duration, and dosing levels required for full-scale implementation.

The Pilot Test Evaluation report and analytical results will be submitted for regulatory review within two months of receipt of the final analytical results.

A pilot study report will be generated as a result of the tasks detailed in this Work Plan. The pilot study report will include field and laboratory data and a comprehensive review of the field study results. Within the conclusions of the report will be recommendations for full-scale implementation of potassium permanganate at the site, if the results indicate potassium permanganate is feasible to remediate groundwater, and the projected duration required for treatment.

9.0 CERTIFICATION STATEMENT

Safety-Kleen Systems, Inc. Service Center
400 Market Street
Oakland, California
EPA ID No. CAD053044053

I certify under penalty of law that this document and all attachments were prepared under my direction or supervision in accordance with a system designed to assure that qualified personnel properly gather and evaluate the information submitted. Based on my inquiry of the person or persons who manage the system, or those persons directly responsible for gathering the information, the information submitted is, to the best of my knowledge and belief, true, accurate, and complete. I am aware that there are significant penalties for submitting false information, including the possibility of fine and imprisonment for knowing violations.



Sara C. Brothers, CPG
Safety-Kleen Systems, Inc.
Senior Project Manager - Remediation

3/1/99
Date

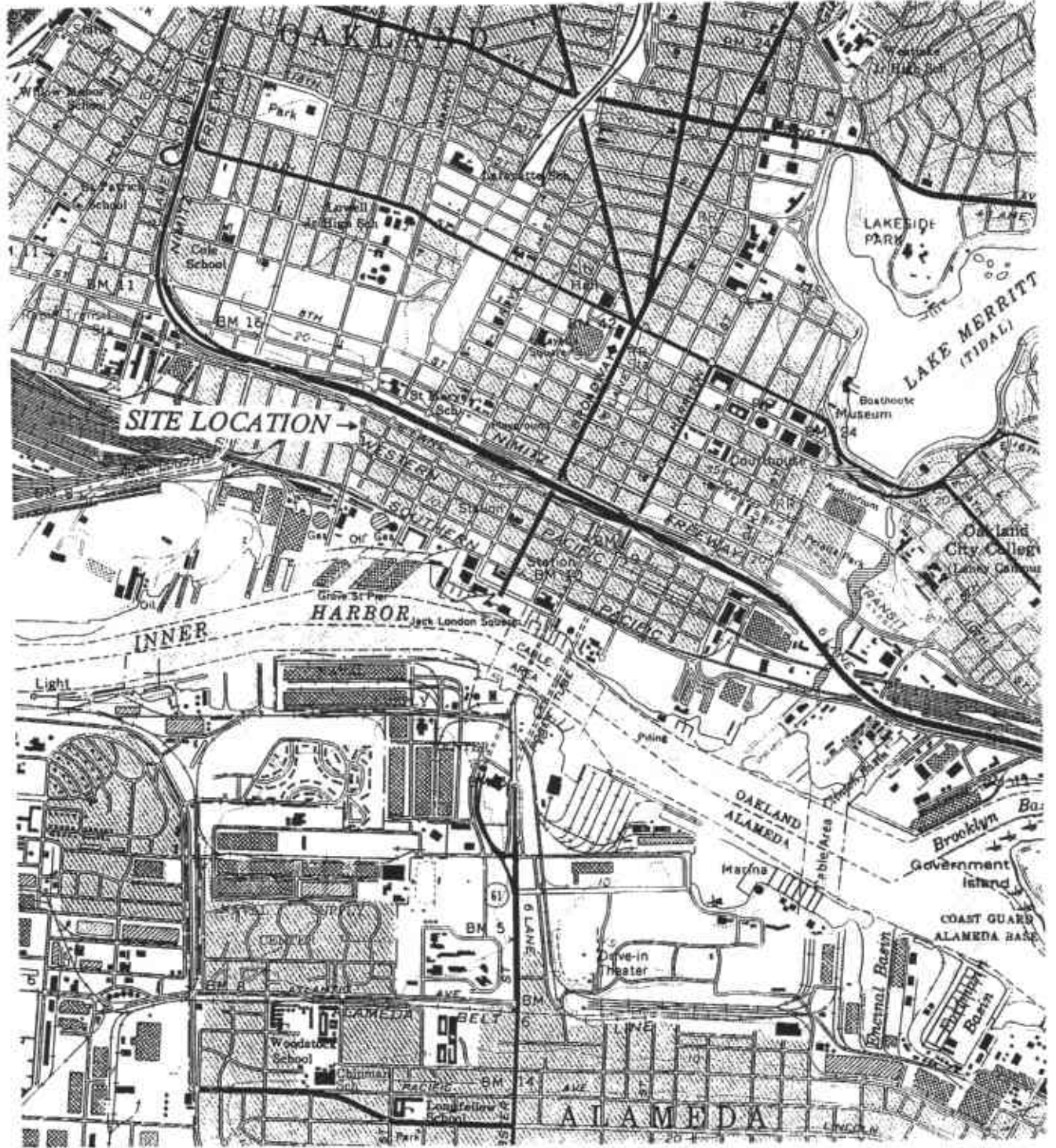
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- California Environmental Protection Agency, Department of Toxic Substances Control, Safety-Kleen Corporation, Revised Hazardous Waste Facility Permit, effective date March 9, 1992.
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- Groundwater Technology, Inc., June 1990, Update Report, Additional Assessment, 404 Market Street, Oakland, California.
- Groundwater Technology, Inc., June 15, 1990, Work Plan For Soil-Vent System and Recovery Well Installation.
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- SECOR (formerly Science and Engineering Analysis Corporation), October 1, 1993, Quarterly Groundwater Monitoring and Soil Vapor Extraction Report, 400 Market Street, Oakland, California.
- United States Geological Survey, topographic map, 7.5-Minute Series, Oakland West Quadrangle, 1959, photo revised 1980.

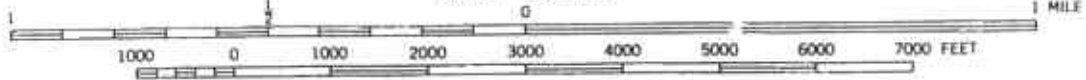
OAKLAND WEST QUADRANGLE

California

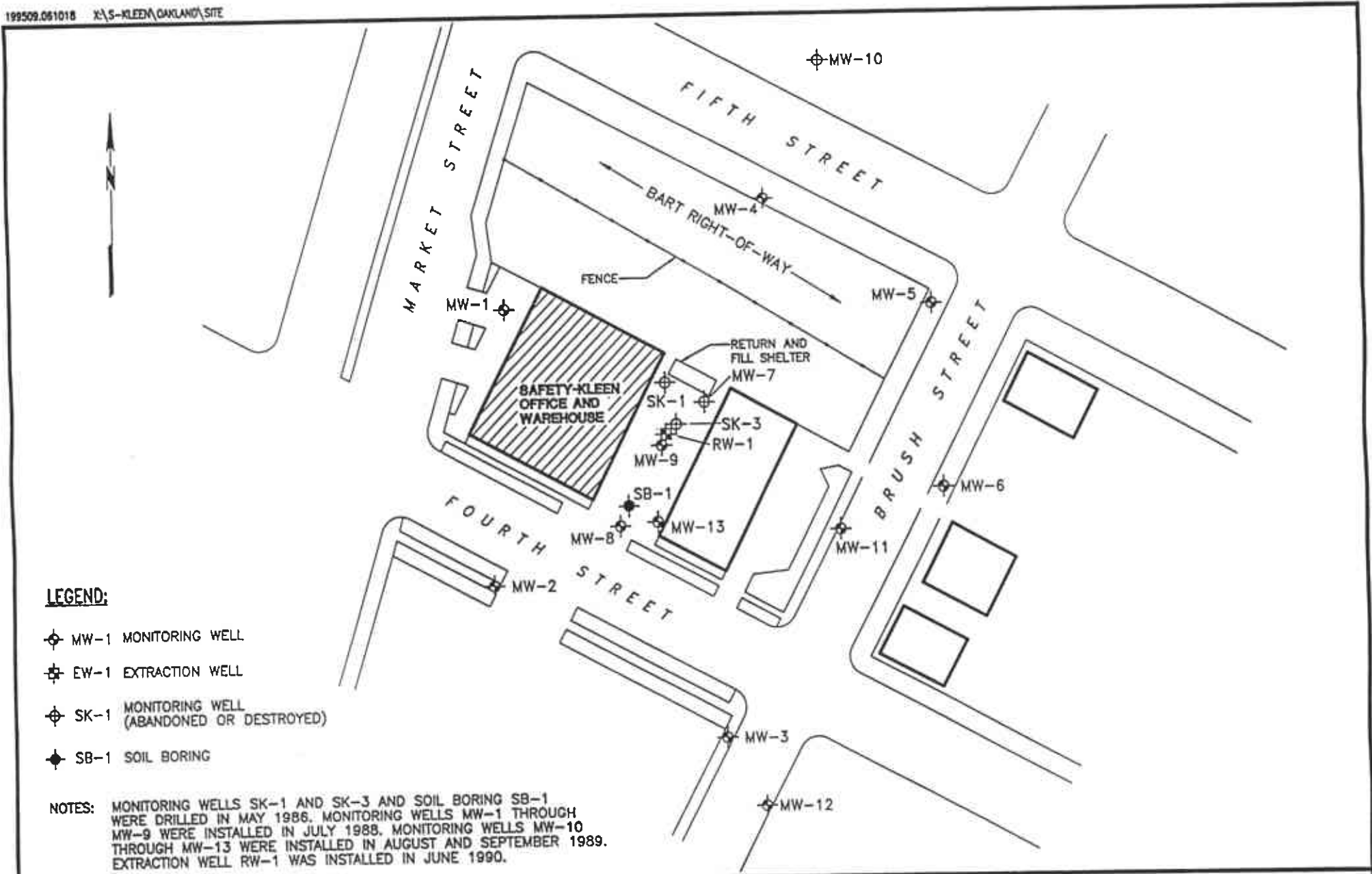
7.5 Minute Series (Topographic)



SCALE 1:24 000



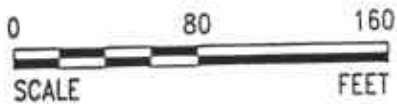
DRAFTED BY: TS	CHECKED BY: GDH	PROJECT NO. 70005-009	FIGURE 1	SECOR 1390 Willow Pass Road Suite 360 Concord, CA 94520
DWG. DATE: 04-05-94	REV. DATE: 06-15-95			
FILE NAME: Oakiand7.F01				



LEGEND:

- ⊕ MW-1 MONITORING WELL
- ⊕ EW-1 EXTRACTION WELL
- ⊕ SK-1 MONITORING WELL (ABANDONED OR DESTROYED)
- ◆ SB-1 SOIL BORING

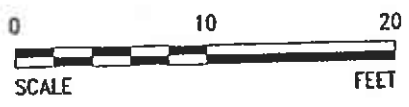
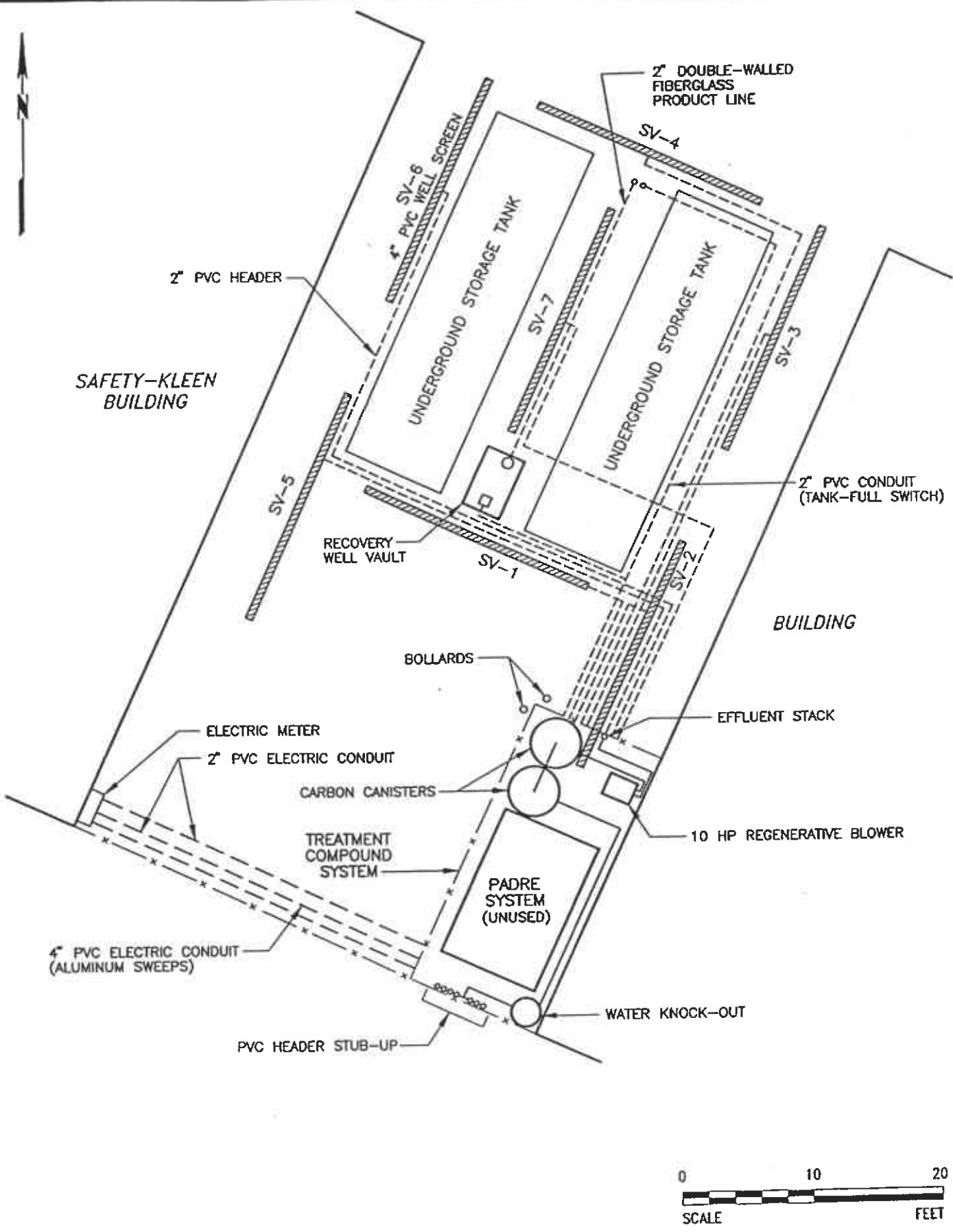
NOTES: MONITORING WELLS SK-1 AND SK-3 AND SOIL BORING SB-1 WERE DRILLED IN MAY 1986. MONITORING WELLS MW-1 THROUGH MW-9 WERE INSTALLED IN JULY 1988. MONITORING WELLS MW-10 THROUGH MW-13 WERE INSTALLED IN AUGUST AND SEPTEMBER 1989. EXTRACTION WELL RW-1 WAS INSTALLED IN JUNE 1990.



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FIGURE 2
SAFETY-KLEEN
400 MARKET STREET
OAKLAND, CALIFORNIA
SITE PLAN

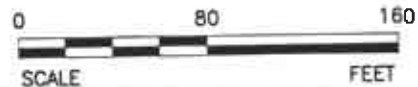
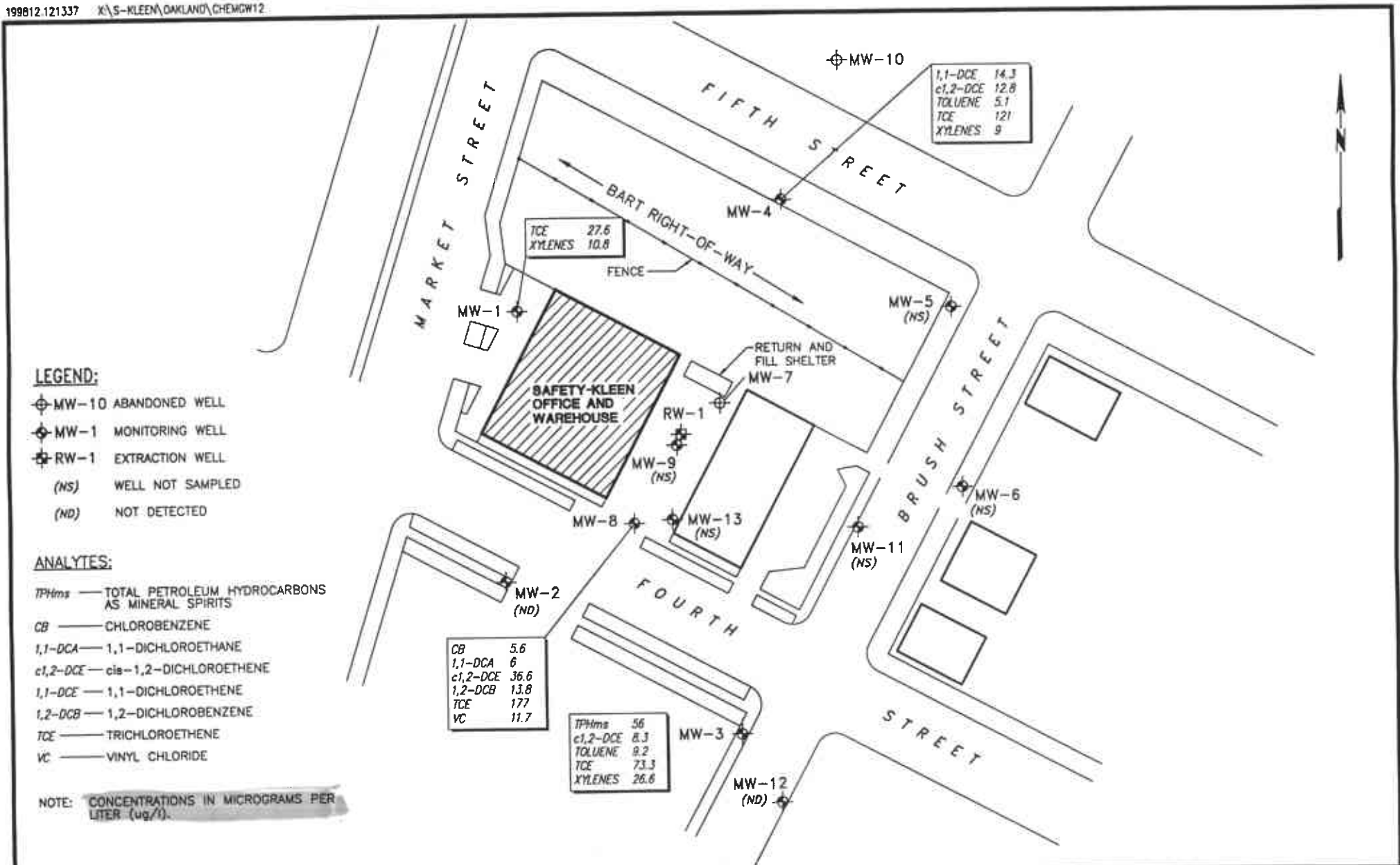


SECOR
INTERNATIONAL
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DRAWN	CCR
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DATE	08DEC95
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FIGURE 3
SAFETY-KLEEN SERVICE CENTER
400 MARKET STREET
OAKLAND, CALIFORNIA
**SOIL VAPOR EXTRACTION
SYSTEM LAYOUT**

199512.071926 X18-KLEEN\OAKLAND\SITE2



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DATE	14DEC98
JOB NO.	70005-009

FIGURE 4
SAFETY-KLEEN SYSTEMS, INC.
400 MARKET STREET
OAKLAND, CALIFORNIA
CHEMICAL DISTRIBUTION IN GROUNDWATER
OCTOBER 12, 1998



Laboratory and controlled field experiments using potassium permanganate to remediate trichloroethylene and perchloroethylene DNAPLs in porous media

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Received 30 December 1994; revised 18 December 1996; accepted 18 December 1996

Abstract

Few proven technologies exist that may be used to treat dense non-aqueous phase liquid (DNAPL) contaminants. In-situ chemical flushing is a proposed technology which consists of flushing DNAPL source zones with a reactive solution to degrade the contaminant mass below ground.

A laboratory and controlled field experimental program was conducted to assess the potential of potassium permanganate (KMnO_4) as a reagent for in-situ DNAPL remediation. The results of laboratory experiments indicated that two common DNAPL contaminants, perchloroethylene (PCE) and trichloroethylene (TCE), were rapidly degraded to chloride and carbon dioxide. Column experiments, using residual PCE flushed with oxidant concentrations as high as 10 g L^{-1} , indicated that chloride could be used as a reaction tracer. From the chloride data, it appeared that the rate of PCE removal from the columns was a complex process dependent upon the kinetics of both dissolution and oxidation.

Two experimental applications of in-situ oxidation were conducted in the Borden aquifer isolated within a 7.5 m^3 double sheet-pile cell. The cell was fitted with injection and recovery wells through which aqueous solutions of KMnO_4 were flushed to oxidize solvent source zones in situ. In the initial experiment, flushing of a 1 L PCE residual source with $10 \text{ g L}^{-1} \text{ KMnO}_4$ at total flow rates of up to 100 L per day, completely removed the source within 120 days. A second experiment, using an 8 L mixture of PCE and TCE slowly allowed to infiltrate into the cell, was

* Corresponding author.

conducted using a system to recycle the oxidant. The oxidant was added at 10 g L^{-1} with a flow of approximately 50 L per day. After 290 days of flushing, it was concluded from the monitoring data that 62% of the initial source (as equivalent chloride mass) had been oxidized and it was evident that oxidation was continuing in the upper third of the cell.

These experiments have suggested that the effectiveness of in-situ chemical oxidation will depend primarily upon the distribution of the DNAPL in the subsurface and its effects upon dissolution. In both experiments, spatial variability of chloride measurements appeared to reflect both the DNAPL location and distribution. © 1998 Elsevier Science B.V.

Keywords: Potassium permanganate; Porous media; DNAPL contaminants

1. Introduction

Trichloroethylene (TCE) and perchloroethylene (PCE) are two chlorinated organic solvents frequently identified as ground water aquifer contaminants (Westrick et al., 1984; Smith, 1990; Plumb, 1991). The US Environmental Protection Agency drinking water standards for each of these compounds is $5 \mu\text{g L}^{-1}$ compared with their solubilities of approximately $1,500 \text{ mg L}^{-1}$ and 240 mg L^{-1} , respectively (Pankow and Cherry, 1996). With five to six orders of magnitude difference between solubility and regulated concentration, the presence of dense non-aqueous phase liquids (DNAPLs), especially in the form of pools in the subsurface, will remain as a very long-term source of contamination until either source containment, isolation or removal has occurred (Mackay and Cherry, 1989; Johnson and Pankow, 1992).

Frequently at sites where DNAPLs are present, pump and treat remediation is selected as a remedial alternative; however, pump and treat approaches to aquifer restoration have demonstrated a distinct lack of success even at sites without DNAPLs (National Research Council, 1994). At sites where DNAPL is present, this approach is primarily limited by low contaminant solubility, contaminant mass storage in low permeability zones, and the relatively large masses of the DNAPL present in the aquifer (Dity and Travis, 1991). The lack of success of pump and treat at these sites has added emphasis to remedial efforts designed to isolate, remove or treat DNAPL sources with the potential benefits of reducing the duration of a subsequent pump and treat containment process and reducing downgradient aqueous phase concentrations.

One example of a mass treatment technology is in-situ oxidation, an approach which consists of flushing a zone of DNAPL contamination with a reactive solution. This technology is conceptually appealing since it combines hydraulic containment of a source zone with contaminant treatment below ground. Various reactive compounds have been suggested including hydrogen peroxide, Fenton's reagent, ozone and potassium permanganate (Cho and Bowers, 1991). To date, documented use of this technology is limited to a single industrial application in which hydrogen peroxide was used to remove an LNAPL release containing 50% formaldehyde with some success (Cowie and Weider, 1986). To our knowledge, the results presented in this paper are the first evaluation of potassium permanganate (KMnO_4) as an in-situ reagent and the first evaluation of in-situ chemical flushing of DNAPL contaminants.

2. Permanganate ion as an oxidant

The use of the permanganate ion (MnO_4^-) to indiscriminately scavenge and oxidize organic contaminants has a long history in both drinking water and wastewater treatment (Steel and McGhee, 1979; Eilbeck and Mattock, 1987), including removal of iron and manganese (Benefield et al., 1982), phenols (Vella et al., 1990), trihalomethane precursors (Colthurst and Singer, 1982) and more recently, TCE (Vella and Veronda, 1992). The reactive properties of MnO_4^- with both organic and inorganic compounds have been described in detail by Stewart (1965) and Lee (1980). Permanganate oxidation of organic compounds is used in the commercial production of various compounds with its most serious limitation being its lack of solubility in most hydrocarbons (Lee, 1980) including PCE and TCE. For example, MnO_4^- oxidation of alkenes is used in the synthesis of the corresponding glycols. In addition to its characteristics as an oxidant, potassium permanganate has a high aqueous solubility (64 g L^{-1} at 20°C (Perry et al., 1984)), a property which would allow for a significant loading rate of oxidant into a contaminated zone. As a solid, KMnO_4 is easily handled and currently costs approximately CDN\$4 per kg.

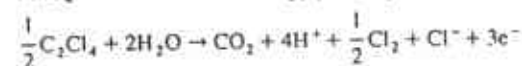
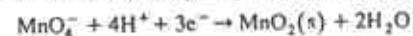
3. Oxidation mechanism

There are few references dealing directly with the oxidation of specific chlorinated organic compounds by KMnO_4 . In general, the existing research has focused on synthesis, rather than destruction, of commercially useful oxidation products from alkenes. Lee (1980) has identified two potential reaction mechanisms for alkene oxidation. Both mechanisms begin with the formation of a hypomanganate diester with subsequent steps generally dependent upon pH and the MnO_4^- concentration. Oxidation of alkenes is generally performed in an aqueous solution due to the fact that KMnO_4 is insoluble in most hydrocarbons without the use of a phase transfer catalyst (Lee, 1980).

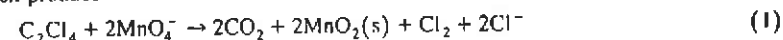
4. Oxidation stoichiometry

Based on laboratory observations and the redox reactions for each compound, overall reactions between KMnO_4 and TCE and PCE were determined. Laboratory observations leading to these equations include the formation of a brown precipitate, determined to be $\text{MnO}_2(\text{s})$, and the evolution of a gas, later confirmed as being CO_2 .

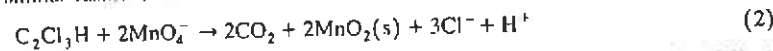
Recognizing that MnO_4^- was reduced to $\text{MnO}_2(\text{s})$ and assuming that the carbon in TCE and PCE was completely oxidized to CO_2 , the following half cell reactions apply:



which produce



In a similar fashion, the reaction for TCE is:



Stoichiometrically, 0.81 kg of Cl^- are produced per kg of TCE oxidized (Eq. (2)). A similar situation exists for PCE except that Eq. (1) suggests the formation of Cl_2 . Based on thermodynamic considerations, it was assumed that the Cl_2 is an intermediate and that Cl^- would be the sole chlorine species present. Therefore, oxidation of 1 kg of PCE should produce 0.86 g Cl^- .

5. Column experimentation: quantifying oxidation with chloride ion

5.1. Experimental outline

Eq. (1) and (2) suggest several possibilities for monitoring the progression of in situ oxidation applications. Some preliminary column experiments indicated that CO_2 in the gas and aqueous phases could be used as a reaction tracer during TCE oxidation but that this would be impractical in natural porous media containing carbonate minerals and natural organic matter. During these experiments significant gas production was observed; in one experiment, the extremely vigorous gas production actually disrupted the soil within the column. It was anticipated that measuring the variation in Cl^- in the effluent during oxidation would provide both a measure of the mass of TCE or PCE oxidized as well an indication of the relative rates of mass removal.

Chloride analyses were performed using an ORION ion selective electrode with a portable meter (ORION Model 720A). Measurements of KMnO_4 concentrations were performed either by titration with thiosulphate or spectrophotometrically (Spectronic 20D). Analysis of TCE and PCE was performed with a Shimadzu GC-9A gas chromatograph

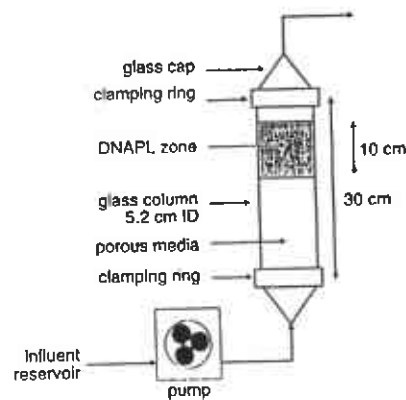


Fig. 1. Column apparatus, source consists of homogeneous PCE residual (1640 mg)

Table 1
Darcy flux and oxidant concentration for experimental columns

	COL 1	COL 2	COL 3	COL 4	COL 5
Darcy flux (cm per day)	42	42	63	68	61
KMnO_4 ($\mu\text{g L}^{-1}$)	10	7.5	10	7.5	0
Oxidant loading ($\mu\text{g cm}^{-2}$ per day)	0.42	0.32	0.63	0.51	0
Total mass removed @ 650 h (%)	121	103	122	119	92
% Mass removed as chloride	92	91	96	93	0

Note: The cross-sectional area of each column was 20.3 cm^2 ; porosity 0.41.

graph with a flame ionization detector and purge and trap unit operated according to EPA Method 601. During these experiments, the detection limits for PCE and TCE analyses were $10 \mu\text{g L}^{-1}$.

To investigate the effects of oxidant concentration and flushing rates upon mass removal, five column experiments were performed using glass columns packed with fine grained sand samples ($\text{foc} = 0.02\%$) from the Canadian Forces Base (CFB) Borden aquifer. In each of the column experiments, the sand was initially saturated with water and 1.0 mL of PCE added as a residual source (volumetric saturation $\sim 1\%$) in the sand. Fig. 1 is a schematic diagram of the experimental apparatus. The columns were subsequently flushed with KMnO_4 solutions at the concentrations and average Darcy fluxes specified in Table 1. Actual flow rates into the columns were variable and were assumed to have produced the principal source of error. One column (COL 5) was flushed only with deionized water to evaluate mass removal by dissolution alone. After the oxidant flush, the columns were flushed with deionized water at the same flow rates.

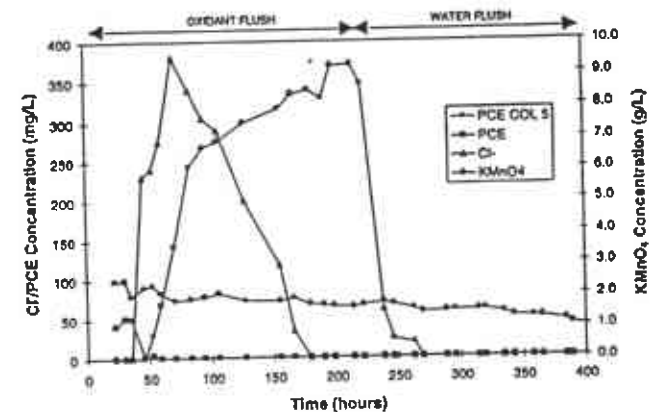


Fig. 2. Column effluent profiles for Cl^- , PCE, input KMnO_4 and effluent KMnO_4 . Also shown are effluent PCE concentrations for COL 5, which was flushed only with deionized water to compare mass removal by dissolution alone.

Control experiments confirmed that oxidation of the PCE was the only source of Cl^- from the columns.

Fig. 2 provides combined Cl^- , KMnO_4 and PCE effluent data for the experiment (COL 3) flushed at the highest oxidant loading and is qualitatively similar to results observed in the other columns. This column was flushed with an aqueous solution of 10

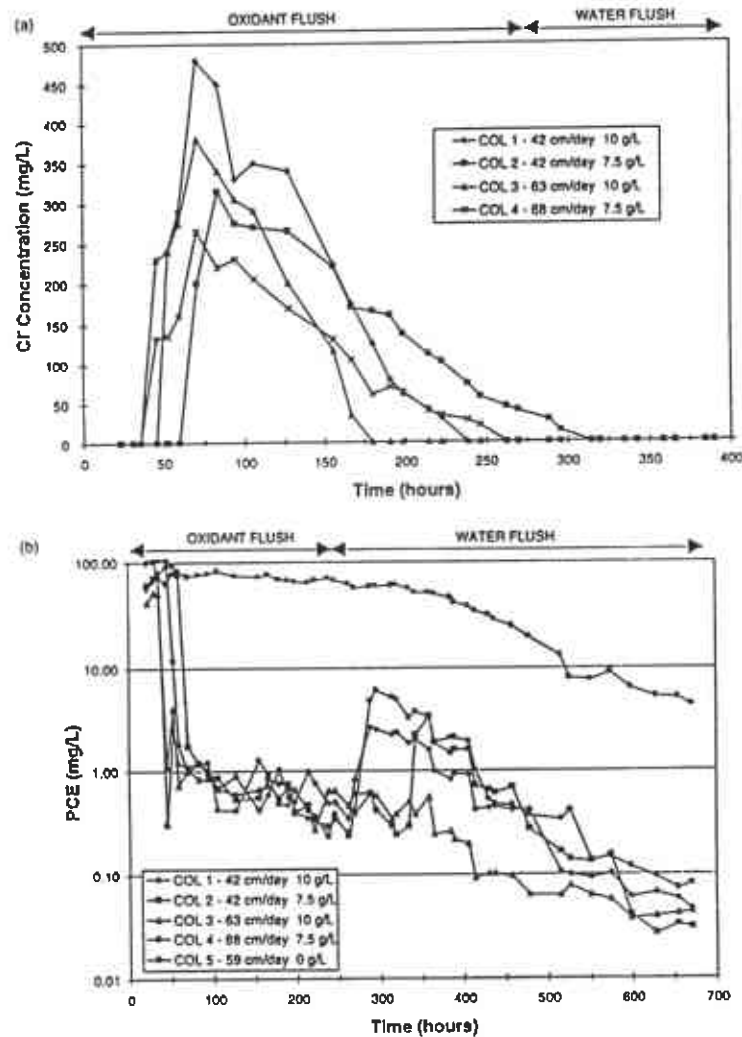


Fig. 3. (a) Effluent chloride concentrations (COL 1-4) and (b) effluent PCE concentrations (COL 1-5).

g L^{-1} KMnO_4 for a period of 214 h and then deionized water for the remainder of the experiment.

In COL 3, PCE in the effluent was initially high ($\sim 50 \text{ mg L}^{-1}$). As the oxidant reached the source zone, Cl^- increased rapidly from non-detectable levels to a peak of 380 mg L^{-1} . When oxidant appeared in the effluent, the PCE concentrations dropped below 1 mg L^{-1} . The concentration of chloride began to decrease after 70 h of flushing and was less than 1 mg L^{-1} after 180 h of flushing. This decline in Cl^- was accompanied by a gradual increase of KMnO_4 in the effluent to above 9 g L^{-1} after 200 h (influent concentration of 10 g L^{-1}). The rate of PCE removal had reduced significantly after approximately 170 h.

In COL 5, the PCE concentration in the effluent from the column reached an initial peak of approximately 100 mg L^{-1} , and then declined slowly to a concentration of approximately 6 mg L^{-1} after 650 h. The dissolution profile from COL 5 is representative of rate limited dissolution for this particular experimental setting.

Effluent Cl^- and PCE effluent concentrations for each of the columns are shown in Fig. 3(a) and (b). All of the columns flushed with oxidant initially produced no effluent Cl^- . Chloride concentrations then rapidly rose to a peak and then slowly declined to non-detectable levels. The two columns flushed at 10 g L^{-1} KMnO_4 producing larger chloride peaks. The initial delay in the appearance of Cl^- and KMnO_4 in the column effluents was attributed to displacement of the initial pore volume of deionized water and consumption of the KMnO_4 through oxidation of organic matter in the sand. In contrast, PCE concentrations in the columns flushed with oxidant were initially high ($\sim 100 \text{ mg L}^{-1}$) and then dropped below 1 mg L^{-1} . In each of these columns, the PCE concentrations tended to increase once the deionized water flush began suggesting that

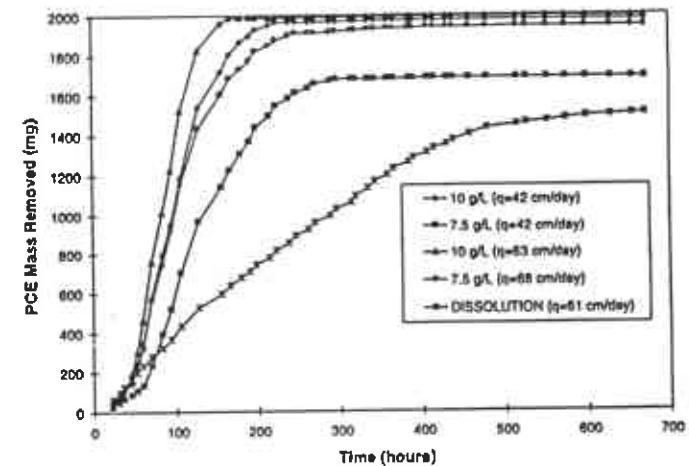


Fig. 4. Accumulated effluent Cl^- mass as a fraction of initial Cl^- mass in column. The accumulated mass removed includes both aqueous PCE and equivalent PCE mass oxidized as calculated from Cl^- data. The initial PCE mass was 1640 mg.

some PCE remained; however relative to the column flushed only with deionized water, effluent PCE concentrations were 1 to 2 orders of magnitude lower.

The accumulated equivalent PCE mass produced from each column is presented in Fig. 4; the mass of the initial PCE source was 1640 mg. The equivalent mass includes both effluent PCE and PCE oxidized calculated from Cl^- in the effluent. The mass balance over-estimates the initial mass of PCE from 103%–122%. This error in the mass balance was attributed mainly to variability in the flow rates.

During the deionized water flush following KMnO_4 addition, the PCE concentration in the effluents from COL 1, 2 and 4 increased from about 0.3 mg L^{-1} to as high as 6 mg L^{-1} then decreased below the detection limit. COL 3, which had the highest oxidant loading, did not experience this rebound. While most of the PCE had been oxidized in situ, a small amount of PCE remained within each column; however, for COL 3 and COL 4 (both flushed at close to the same flow rate as the dissolution control) the final effluent PCE concentrations were about 1% of those in COL 5.

6. Field experimentation

6.1. Experimental cell details

Two pilot scale experiments were performed at the CFB Borden research site in an unconfined, shallow aquifer consisting of a glaciolacustrine sand (Bolha, 1986). The sand is predominantly medium to fine grained and, while relatively homogeneous, contains numerous horizontal bedding features varying in thickness from millimeters to a few centimeters (Ball et al., 1990; Poulsen and Kueper, 1992). The mean hydraulic conductivity of the sand is $7.2 \times 10^{-3} \text{ cm s}^{-1}$ (Sudicky, 1986). The experimental cell, consisting of double-walled, sealed joint sheet piling (Starr et al., 1992) extended from the surface down to a clay aquitard at a depth of approximately 2.5 m (Fig. 5). The pore volume of the cell, estimated from the sand porosity of 0.33 (Ball et al., 1990), was approximately 2.48 m^3 .

Six injection and six extraction wells (2 in ID PVC) were located at opposite ends of the cell as shown; these were screened at upper, intermediate, and lower depths with each pair of well screens extending over one third of the depth. Also shown in Fig. 5 are the multilevel samplers which allowed collection of small volume samples from various points with the cell. The multilevel piezometers consisted of 0.06 in ID Teflon® tubes attached at 1 foot intervals to a central 0.5 in OD PVC pipe. The instrumentation was installed by simultaneously driving and jetting a 3 in ID steel casing to the required depth with a hand-held vibrating hammer, inserting the well casing or multilevel stem, withdrawing the larger steel casing and allowing the formation to collapse around the instrument.

6.2. Sampling methods

Sample collection from the multilevels was performed by connecting individual sample points to a 250 mL Erlenmeyer flask through a stopper. A vacuum was applied to the flask using a 50 mL syringe. Typically, 75–100 mL of sample were collected. Part of this volume was decanted into an 8 mL vial with Teflon® lined septa for TCE

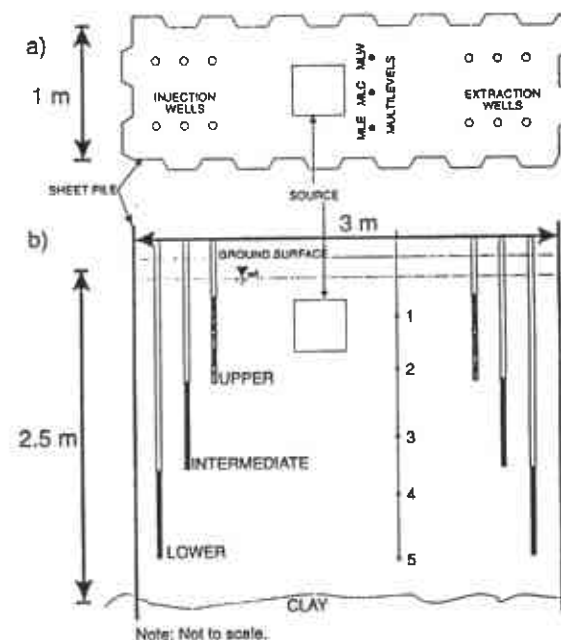


Fig. 5. Schematic diagram of experiment cell at CFB Borden field site, including (a) plan view and (b) cross-section, illustrating location of instrumentation and NAPL sources.

and PCE analysis. A small quantity of granular sodium thiosulphate was added to reduce any KMnO_4 and prevent further solvent oxidation. The remaining volume was stored in a 40 mL EPA vial for Cl^- analysis. Sample analyses were conducted using the previously mentioned analytical methods.

7. Experiment I: homogeneous residual source

The DNAPL source for Experiment I consisted of 1 L (1.64 kg) of PCE which was mixed with soil taken from a $0.3 \text{ m} \times 0.3 \text{ m} \times 0.35 \text{ m}$ block below the water table. The soil:DNAPL mixture was replaced in the excavated block (Fig. 5). The residual DNAPL saturation was estimated to be 8% (v/v). The cell was subsequently flushed with a 10 g L^{-1} aqueous solution of KMnO_4 through the injection wells; effluent was withdrawn from the extraction wells. Constant head was maintained in the injection wells by siphoning from a constant head reservoir into each well. Flow rates were controlled by a peristaltic pump at the extraction wells. Initially, both the upper and intermediate extraction wells were pumped at a total flow rate of approximately 100 L per day. After monitoring confirmed that oxidation was occurring only in the upper third of the cell, pumping from the intermediate extraction wells was stopped at 1200 h with the new flow rate of 50 L per day from the upper wells. The cell was flushed with oxidant

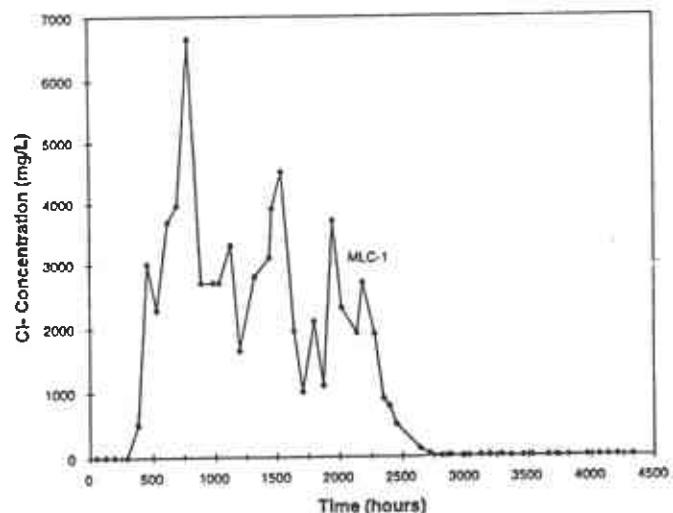


Fig. 6. Chloride concentrations observed at MLC-1, directly downgradient of the residual PCE source.

solution for 120 days and then with water for a further 60 days to displace the remaining oxidant and reaction products. Effluent from the cell was continuously treated to remove residual oxidant and aqueous phase PCE.

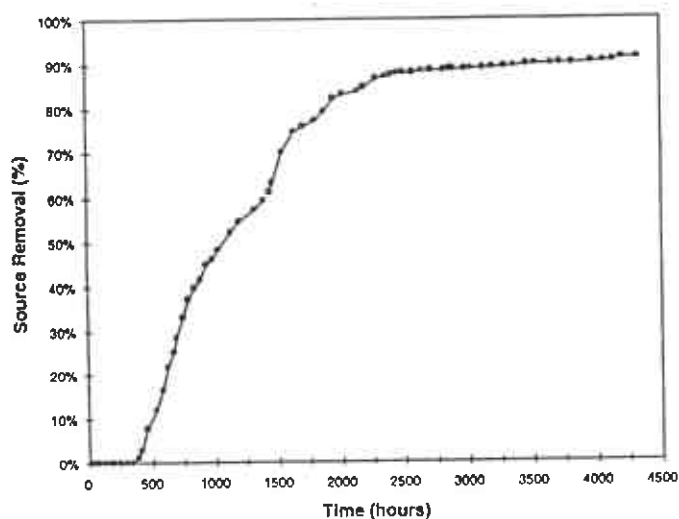


Fig. 7. Accumulated PCE mass destruction calculated based on observed chloride concentrations.

Chloride monitoring from the multilevel piezometers indicated that Cl^- was produced only in the upper third of the cell. After approximately 300 h of flushing, a rapid increase in Cl^- was observed in MLC-1 (Fig. 6). Over the remainder of the experiment, Cl^- concentrations at this point gradually declined to non-detectable levels. Using the Cl^- data from the extraction wells, the cumulative mass of effluent Cl^- was determined to be 1486 g or 91% of the chloride content of the initial source mass (Fig. 7).

Several other quantitative measures were used to evaluate the effectiveness of this experiment. PCE was not detected during the post-oxidation water flush. As well, a core was removed from the source zone after the water flush from which subsamples were taken and analyzed for their PCE content. Solvent concentrations in these subsamples were below the method detection limit ($< 0.0003\%$ w/w).

8. Experiment II: heterogeneous NAPL source

Experiment II had a mixture of PCE and TCE as a source; source emplacement was designed to simulate a slow leak release. Six 2.5 cm ID stainless steel pipes, 1.0 m long and equipped with drive points, were driven to a depth of 0.25 m in the centre of the cell in the same location as the Experiment I source. Equal masses of TCE and PCE (6.19 kg each, 8.0 L in total) were mixed with Sudan IV and distributed equally into the six source points over a period of 9 days. Volatilization of the TCE/PCE mixture was minimized by adding it below the water table; however, some minor loss from the separatory funnels containing the mixture was likely. The DNAPL mixture was allowed to migrate within the cell for an additional 10 days before beginning in-situ KMnO_4 oxidation.

No effort was made to determine the distribution of the DNAPL within the cell; however, DNAPL was withdrawn from several of the multilevel sampling points throughout the course of the experiment. Initially, pure phase was evident in all the MLW and MLC sampling points but as treatment proceeded, free product persisted at only the lowest point of the centre multilevel (MLC-5).

8.1. Treatment system

The treatment system was designed to supply KMnO_4 at a concentration of 10 g L^{-1} through all six injection wells at a total flow rate of 48 L per day using the system of peristaltic pumps and a constant head reservoir as in Experiment I.

In Experiment I, the effluent eventually contained unused oxidant at concentrations close to 10 g L^{-1} . An oxidant recycle system was used in Experiment II to reduce the amount of oxidant used and to eliminate the need for continuous effluent treatment. In this system (Fig. 8), effluent was pumped through a coarse cartridge filter and discharged to a equalization and settling tank for removal of suspended $\text{MnO}_2(\text{s})$ and other solids. The main effluent line was drained by gravity to the constant head injection reservoir. A sample loop from the main effluent line ran through a spectrophotometer and was used to monitor KMnO_4 concentrations. The spectrophotometer provided an input to a PID controller. In turn, the controller ran a peristaltic pump which diverted a fraction of the main effluent flow to a column packed with crystalline KMnO_4 . The

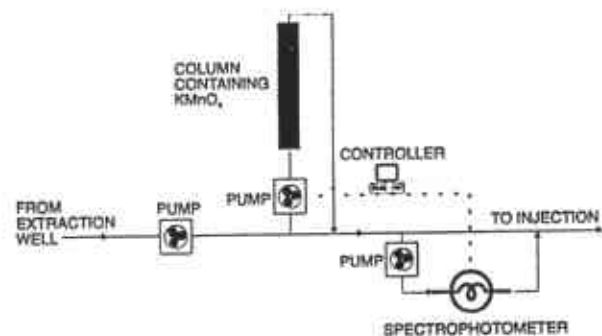


Fig. 8. Treatment schematic for Experiment II oxidant recycle system.

discharge from the column produced an oxidant solution near solubility (64 g L^{-1} at 20°C (Perry et al., 1984)). This stream was mixed back into the main effluent line before the spectrophotometer sample loop.

8.2. Cl^- concentration profiles in multilevels

Fig. 9 presents data from MLC. Low background Cl^- concentrations (generally less than 20 mg L^{-1}) were observed prior to KMnO_4 addition. After KMnO_4 addition, substantial increases in Cl^- concentration were observed. At three levels (MLC-2,

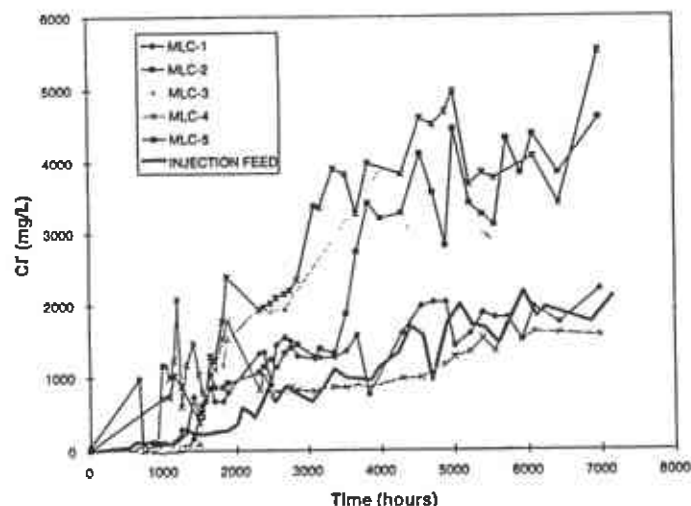


Fig. 9. Chloride concentrations observed in MLC (MLC 1 is the shallowest; MLC 5 is the deepest). The heavy line represents the variation of Cl^- in the injected oxidant solution.

MLC-3 and MLC-5), concentrations exceeded 3000 mg L^{-1} , indicating that significant oxidation was occurring adjacent to these points.

MLC-1 and MLC-4 exhibited little evidence of oxidation. Each experienced a gradual increase in Cl^- but this was owing principally to Cl^- in the recycled KMnO_4 solution. Cl^- concentrations at each of these two points were generally similar to the profile of injection feed concentrations indicating relatively little DNAPL oxidation at these depths.

8.3. Cl^- and solvent concentration profiles in extraction wells

PCE concentration data from the extraction wells are presented in Fig. 10; the data points are averages for the pair of wells at each depth. TCE concentrations (not shown) were generally similar but slightly higher. Some trends are evident in spite of high variability in the data. The highest concentrations of both solvents were observed in the upper wells. From 2000 to 2500 h, the concentrations of PCE were in the 10 to 50 mg L^{-1} range. During this time, the effluent from the extraction wells was nearly colourless indicating that most of the KMnO_4 had been consumed. Beyond this time, KMnO_4 concentrations began to increase in the effluent with a corresponding reduction in the PCE concentrations.

The PCE and TCE concentrations declined with time and after approximately 6000 h, remained at concentrations less than 0.01 mg L^{-1} . At this point, the effluent had high KMnO_4 concentrations approaching the injected concentration.

Chloride concentrations (Fig. 11) in all of the extraction wells increased over time owing to the recycling of the Cl^- in addition to the oxidant. The changes in concentration relative the concentration of Cl^- injected in the cell provide some clue to the location of DNAPL mass. The intermediate and lower extraction well profiles are similar to the injection feed profile suggesting that little mass removal is occurring in the

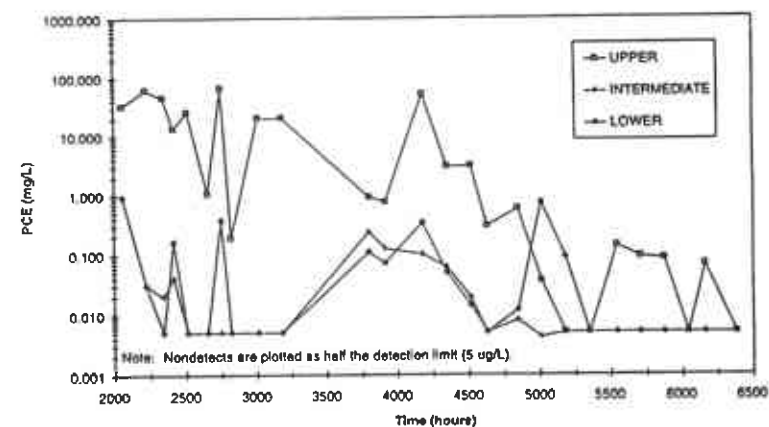


Fig. 10. Effluent PCE in the three pairs of extraction wells (highest relative concentrations in the upper pair).

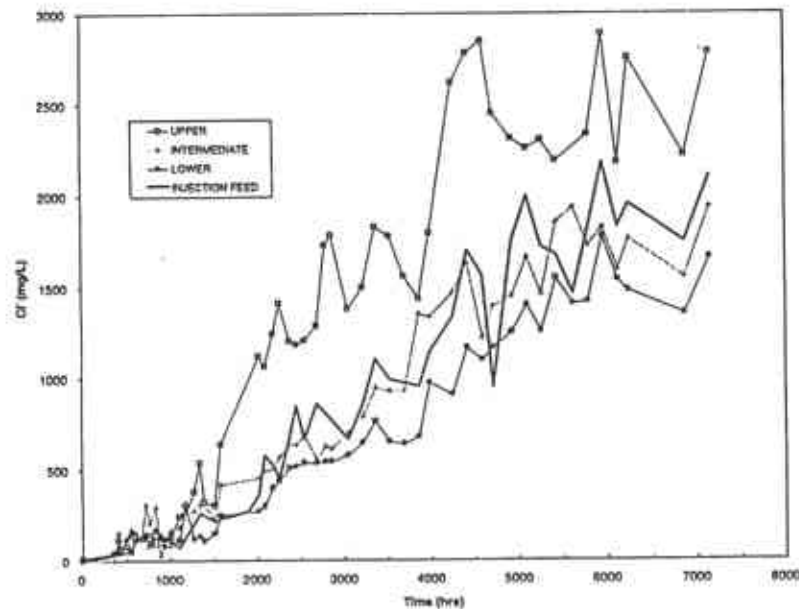


Fig. 11. Chloride concentrations observed in the extraction wells.

lower two thirds of the cell; however, up to the end of the oxidant flush, the Cl^- concentration in the upper extraction well is higher than the injection feed indicating that some solvent mass is still being oxidized.

8.4. Chloride mass balance

Mass balance calculations based on Cl^- production were used to estimate the extent of DNAPL oxidation. With a single pass system, such as that used in Experiment I, the concentration of Cl^- in the effluent from the extraction wells was readily converted to an equivalent mass of PCE oxidized. However, the recycle system used in Experiment II complicated the mass balance calculations because of the recycling of Cl^- back into the cell.

In addition, problems with the reinjection equipment during the initial stages of treatment resulted in periodic effluent losses from the system. It was estimated that 1.1 kg of Cl^- or 11% of the initial Cl^- mass was lost in this way.

An approximate method was used to estimate the mass of DNAPL oxidized based on Cl^- release. The averages of the last five effluent and the feed concentrations shown in Fig. 12 were assumed to represent the average Cl^- concentration in the entire cell. The total pore volume of the cell plus the liquid volume in the above ground treatment system, was estimated to be 2800 L. Based on this average, it was determined that

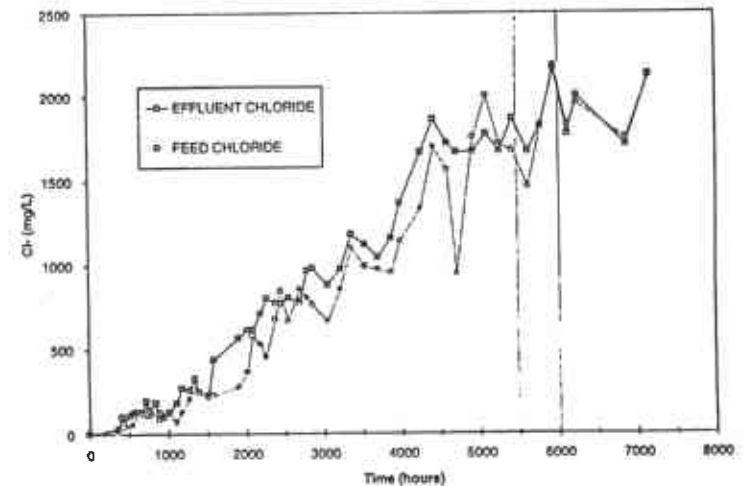


Fig. 12. Average effluent and injection feed chloride concentrations used to estimate total chloride mass in system.

approximately 51% of the Cl^- content of the original solvent source was present in this volume. Including the 11% Cl^- loss, approximately 62% of the initial mass of chlorine had been released by the oxidant flush.

9. Discussion

While in-situ oxidation removed substantial DNAPL mass in both field experiments, it is likely that the subsurface distribution of DNAPL had a significant effect on the rates of mass removal. In Experiment I, the residual PCE source was rapidly and completely oxidized, a reflection of the homogeneous distribution of the DNAPL as a residual with a relatively large surface area:volume (A:V) ratio which would allow rapid dissolution. As well, the aqueous phase permeability in the source area would be high relative to the permeability of source zones with high NAPL saturations. In more typical DNAPL sources, such as that used in Experiment II, non-wetting phase saturations would be highly variable and could possibly include pooled DNAPL above slight permeability contrasts. For example, in an experimental PCE release at a nearby location, PCE flow was found to be controlled by millimeter scale sand bedding structures with non-wetting phase saturations ranging from 1% to 38.1% (Kucper et al., 1993). Experiment II, containing a variable DNAPL distribution, would likely have some fraction of the solvent source present in both high and low saturations. The low saturations would be readily oxidized (as in Experiment I) but mass removal of high saturation zones would be slow owing both the lower aqueous phase permeability and lower A:V ratios. In the extreme case, where all the DNAPL is present as pools above low permeability zones

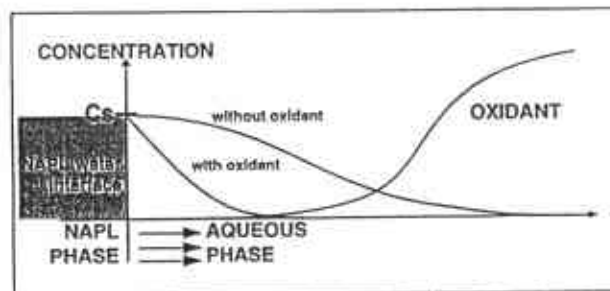


Fig. 13. Conceptual model describing mass removal by in-situ chemical oxidation.

and is occupying almost the entire pore space, mass removal would be limited by weak dispersive processes, resulting in lower mass removal from the source zone than achievable by advectively dominated flushing.

Successful prediction of overall rates of mass removal would require rate expressions for both non-equilibrium dissolution and oxidation. In the conceptual model (Fig. 13) proposed in this work to describe mass removal rates, dissolution mass transfer, driven primarily by aqueous phase PCE/TCE concentration gradients, is enhanced by the oxidation reaction which increases these gradients. As the aqueous solvent gradient is increased, the dissolution mass flux is increased. Simultaneously, the concentration gradient of the oxidant would be increased, causing an increase in oxidant mass flux towards the DNAPL:water interface.

The ability of in situ oxidation to remove PCE was clearly demonstrated in Experiment I. Based on the Cl^- mass balance, greater than 90% of the 1.64 kg emplaced mass was oxidized in 120 days; however, it was inferred from source sampling that 100% of the mass had actually been removed. The peak PCE concentration observed in the extraction wells at the beginning of this experiment prior to oxidation was 18 mg L^{-1} . Assuming that this effluent concentration remained constant, removal of the entire source by water flushing alone would require, at a minimum, 900 days. In agreement with the conceptual model of dissolution and oxidation as parallel kinetic processes, the oxidant flush was able to accelerate dissolution of this source by increasing the concentration gradients of both the dissolved phase solvent and the oxidant. It was evident from the Cl^- profiles that mass removal tailed off after the peak, an indication that mass transfer rates during the oxidant flush were decreasing as DNAPL mass was removed. This would suggest that the mass transfer rate expressions currently in the published literature (e.g. Powers et al., 1994; Geller and Hunt, 1993; Guiguer and Frind, 1994) might be applied to estimate dissolution mass transfer during an oxidant flush.

The release of Cl^- provided a measure of the spatial extent of source. During Experiment I, Cl^- production occurred only in the upper third of the cell zone and the treatment process was adjusted to limit flow to this area alone. In Experiment II, most of the oxidation again appeared to occur in the upper third of the cell based on the

extraction well Cl^- profiles. The Cl^- concentrations in the multilevel samplers generally supported this; however, the highest Cl^- concentrations were observed in MLC-5. This same multilevel contained pure phase during the entire experiment. These data suggest that during the DNAPL release at the beginning of the experiment, a portion of the solvent mixture moved laterally from the injection points, migrated down the multilevel stem and became immobilized at or below MLC-5. This is supported by other observations. During the experiment, Cl^- concentrations in the lower extraction wells, covering the vertical position of MLC-5, were only slightly different from the feed concentrations implying that little oxidation was occurring in the bottom third of the cell. This is consistent with the possibility of a small amount of DNAPL located right at the multilevel MLC 5 being oxidized to produce high localized Cl^- concentrations but only a small amount of Cl^- mass in the extraction wells. Short-circuiting down multilevel stems was also observed by Kueper et al. (1993).

Recycling of the oxidant was an effective method of reducing the amount of oxidant required and the degree of effluent treatment. Experiment I used approximately 80 kg of oxidant while Experiment II, with a substantially larger source mass, used almost 50 kg.

During Experiment I, it was expected that organic material and reduced mineral species in the Borden sand ($\text{foc} = 0.027\% \text{ w/w}$, Ball et al., 1990) would consume oxidant. The oxidant demand of the Borden sand in the cell was estimated, based on effluent KMnO_4 data (not shown) from Experiment I to be at most, $7 \text{ kg KMnO}_4 \text{ m}^{-1}$ Borden sand.

10. Application of in-situ oxidation at industrial sites

Experimentation with KMnO_4 has been limited to oxidation of TCE and PCE. While some other NAPL contaminants may be oxidizable (for example, other chlorinated alkenes), it is probable that many compounds will either be largely resistant to permanganate oxidation or oxidized in secondary organic compounds which may also be hazardous. This factor may make permanganate an unsuitable oxidant at field sites contaminated with solvent mixtures other than PCE and TCE. At field sites with complicated hydrogeology, the DNAPL source is likely to be spatially large with a complex distribution; a comprehensive site characterization program will be required to design of an injection system capable of supplying oxidant to the entire source while minimizing the volume of the treatment zone. At many sites, some DNAPL will be isolated from advective flow causing mass removal to be limited by diffusion of oxidant into that zone. In these zones, it is possible that mass removal by oxidation will be faster than technologies such as cosolvent/surfactant flushing, owing to the increased concentration gradients proposed in the conceptual model. In many cases, it may be that the application of in situ oxidation will rapidly remove the fraction of the DNAPL mass which has the largest driving potential for dissolution (large area to volume ratios in high permeability zones). Removal of this fraction could result in significant lowering of aqueous concentrations with only a modest reduction in DNAPL mass, which would be advantageous from both economic and risk based perspectives.

11. Summary and conclusions

Laboratory and pilot scale field experiments were performed to evaluate the effectiveness of KMnO_4 flushing as a means of DNAPL source removal through in-situ oxidation.

Column experimentation indicated that using the reaction product Cl^- was an effective means of following the progress of the oxidation reaction. Calculated mass balances based on Cl^- tended to overpredict mass removal; however, it was inferred from post-oxidation aqueous phase PCE concentrations that nearly complete removal of the PCE source was achieved. As well, mass removal was significantly faster and aqueous phase PCE concentrations were one to two orders of magnitude lower than with aqueous flushing alone.

Two field experiments were completed within a section of the CFB Borden aquifer isolated by double walled sheet piling. In each experiment, monitoring of the process was accomplished by measurements of Cl^- concentrations in multilevel piezometers and extraction wells. In Experiment I with a emplaced residual PCE source, the oxidant flush removed 100% of the DNAPL mass, as determined by aqueous phase concentrations, a chloride mass balance, and source zone core samples. In Experiment II, using a heterogeneous source produced by slowly leaking PCE and TCE into the field cell, about 60% of the DNAPL mass was removed from the source. Several factors appeared to control the effectiveness of in situ oxidation at the field scale. The process of dissolution is the principal determinant of DNAPL mass removal rates. It was clear that the rate of dissolution during an oxidant flush is much more rapid than during a water flush. Linked to the dissolution process is the distribution of the DNAPL and geologic heterogeneity. Complex distributions will require careful site characterization to design an effective oxidant injection system that is capable of delivering oxidant to the entire source zone.

Oxidant recycling was determined to be an effective and practical method of reducing both the total amount of oxidant required as well as the need for effluent treatment.

Chloride monitoring during each experiment was used to estimate the amount of mass destruction and also provided some indication of the location of the DNAPL.

The in situ oxidation technology has potential to be an effective means of removing DNAPL mass at rates much more rapid than conventional pump and treat strategies. It is unlikely that in-situ oxidation could ever remove 100% of the contaminant mass at an actual field site within a realistic time frame; however, it is feasible that rapid removal of the more accessible DNAPL will result in lower plume concentrations subsequent to the chemical flush and reduce the time required for a subsequent pump and treat system. Further work characterizing the dissolution process from various DNAPL distributions during an oxidant flush is presently ongoing to adequately address both these possibilities.

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Optimization of pump–treat–inject (PTI) design for the remediation of a contaminated aquifer: multi-stage design with chance constraints

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Abstract

A large scale groundwater remediation project using pump-and-treat (PAT) or pump–treat–inject (PTI) cannot be designed as a single time-step operation, because of uncertainties associated with the system. The changes in concentrations in reality may differ significantly from predicted ones. Instead, a multi-stage decision process is formulated and solved as a two-level hierarchical optimization model. Cost serves as the objective function, while contaminant concentration and total cleanup time are constraints. The entire cleanup time is divided into several stages. The number of wells for both pumping and injection is treated as a decision variable in each design stage. At the basic level, well locations and pumping/injection rates are sought so as to maximize mass removal of contaminants. At the upper level, the number of wells for pumping and injection is optimized, so as to minimize the cost, taking maximum contaminant level (MCL) as a constraint. Indices for the equivalent centroid and areal extent of a contaminant plume are proposed and used to initiate well locations at each design stage. © 1998 Elsevier Science B.V.

Keywords: Optimization; Aquifer; Contamination; Remediation; Pump–treat–inject

1. Introduction

During the last decade, much attention has been focused on the remediation of contaminated aquifers. One of the most common techniques for the cleanup of a

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