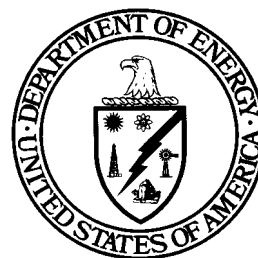




Summary Report DOE/EM-0496

In Situ Chemical Oxidation Using Potassium Permanganate

Subsurface Contaminants
Focus Area



Prepared for
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Office of Environmental Management
Office of Science and Technology

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In Situ Chemical Oxidation Using Potassium Permanganate

OST/TMS ID 167

Subsurface Contaminants
Focus Area

Demonstrated at
Portsmouth Gaseous Diffusion Plant
Piketon, Ohio



Purpose of this document

Innovative Technology Summary Reports are designed to provide potential users with the information they need to quickly determine whether a technology would apply to a particular environmental management problem. They are also designed for readers who may recommend that a technology be considered by prospective users.

Each report describes a technology, system, or process that has been developed and tested with funding from DOE's Office of Science and Technology (OST). A report presents the full range of problems that a technology, system, or process will address and its advantages to the DOE cleanup in terms of system performance, cost, and cleanup effectiveness. Most reports include comparisons to baseline technologies as well as other competing technologies. Information about commercial availability and technology readiness for implementation is also included. Innovative Technology Summary Reports are intended to provide summary information. References for more detailed information are provided in an appendix.

Efforts have been made to provide key data describing the performance, cost, and regulatory acceptance of the technology. If this information was not available at the time of publication, the omission is noted.

All published Innovative Technology Summary Reports are available on the OST Web site at <http://ost.em.doe.gov> under "Publications."

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SECTION 1

SUMMARY

Technology Summary

Problem

Groundwater and soils contaminated with organic compounds, such as solvents, are often difficult to remediate. The standard technology, pump and treat at the surface, is known to be expensive and to take years to complete. At some sites, low permeability zones contain a large percentage of the contaminant mass. The contaminants held within these zones are often not well accessed by standard pump and treat systems, thus prolonging the time required for remediation of the entire site and increasing the costs of remediation. Alternative technologies that can better access, especially source zones containing dense non-aqueous phase liquids (DNAPLs), to more efficiently remediate subsurface aquifers and rapidly treat the contaminants have recently been investigated.

How It Works

- In situ chemical oxidation is a developing class of remediation technologies in which organic contaminants are degraded in place by oxidants delivered to the subsurface. Successful implementation of this technology requires an effective means for dispersing the oxidant to the subsurface contaminated regions.
- In Situ Chemical Oxidation Using Potassium Permanganate (KMnO_4) for soil and groundwater treatment has been demonstrated at a number of sites on the following organics:
 - chlorinated solvents (alkenes such as trichloroethylene [TCE] and perchloroethylene [PCE]); and
 - naphthalene and pyrene.
- In Situ Chemical Oxidation Using KMnO_4 through recirculation, the subject of this report, is the technique of delivering aqueous oxidant through multiple horizontal and/or vertical wells. In Situ Chemical Oxidation Using KMnO_4 used horizontal wells to provide improved access to a subsurface contaminant plume that contains TCE. Groundwater was extracted from one of the horizontal wells; KMnO_4 was added to oxidize the contaminants in the groundwater, which was then reinjected into the other parallel horizontal well.

Potential Markets

- Chemical oxidation using KMnO_4 has been widely used for treatment of pollutants in drinking water and wastewater applications for over 50 years. In situ chemical oxidation has more recently been used to remediate hazardous waste sites with soils and groundwater contaminated with organics utilizing 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.
- In Situ Chemical Oxidation using KMnO_4 is a rapid and cost-effective treatment when used to treat DNAPL source zones or zones of high residual contamination.
- In Situ Chemical Oxidation Using KMnO_4 is an alternative approach for sites where the physical disruption of contaminated soils is not desirable, feasible, or necessary.
- Most DOE sites contain groundwater plumes that contain organics, with source zones, that could be treated with In Situ Chemical Oxidation Using KMnO_4 .



Advantages Over Baseline

- In Situ Chemical Oxidation Using KMnO_4 is cheaper than the baseline pump and treat technology for certain applications, because the time of remediation can be significantly reduced by targeting treatment of the DNAPL source zone.
- In Situ Chemical Oxidation Using KMnO_4 can also be cheaper than alternative technologies such as deep soil mixing, as larger volumes of soil can be treated with multiple oxidant dosings.
- In Situ Chemical Oxidation Using KMnO_4 is advantageous over the baseline and alternative technologies because it generates innocuous by-products (carbon dioxide and manganese dioxide solids), allows introduction of large volumes of oxidant solution; the recirculation process provides for better oxidant control within the treatment area as compared to well injection alone.

Demonstration Summary

- In Situ Chemical Oxidation Using KMnO_4 to treat TCE present as DNAPL and as a dissolved plume at the X-701B facility was demonstrated at the Portsmouth Gaseous Diffusion Plant (PORTS) in the spring of 1997.
- The demonstration at PORTS was implemented using a pair of parallel horizontal wells with 200-foot (ft) screened sections located in a 5-ft thick silty, gravel aquifer within the center of a groundwater plume originating from a known source of DNAPL. Crystalline KMnO_4 was added to groundwater extracted from the upgradient well and re-injected into the downgradient well approximately 90 feet from the extraction well.
- Oxidant solution (~2% KMnO_4) was recirculated through the horizontal wells for approximately one month. Subsequent injection of KMnO_4 into a nearby vertical well was conducted for 8 days to enhance uniform delivery of the oxidant in the region between the horizontal wells.
- The stratigraphy at the X-701B site consists of two unconsolidated units overlying bedrock:
 - the Minford silt and clay with a thickness of 25 to 30 ft;
 - the Gallia sand and gravel, which has a thickness varying from 2 to 10 ft (5 to 6 ft within the region between the horizontal wells). The Gallia sand and gravel was the target aquifer to be treated during this demonstration.

Key Results

- The recirculation concept to introduce oxidant into the subsurface was shown to be viable.
- Oxidant injection without extraction is feasible; however, extraction provides enhanced control of the subsequent movement of the oxidant after its release.
- Lateral and vertical heterogeneities within the aquifer significantly impacted uniform delivery of the oxidant through the horizontal wells.
- Significant reductions in TCE were measured in both groundwater and soil samples in areas where the oxidant was delivered. During post-treatment sampling, TCE was not detected (< 5 parts per billion [ppb]) in samples collected from the monitoring wells and soil borings in locations where the oxidant had permeated. However, because oxidant delivery was not uniform, TCE was not reduced to non-detectable levels in all groundwater and soil samples.
- A system for handling precipitated solids may need to be incorporated when high concentrations of oxidant are recirculated.



- The demonstration at PORTS (Figure 1) was conducted by Oak Ridge National Laboratory. It was sponsored by the U. S. Department of Energy (DOE), Office of Science and Technology, and the DOE Portsmouth Site Office. This demonstration was conducted as part of a larger ongoing project with contributions from: Bechtel Jacobs Company (formerly Lockheed Martin Energy Systems), Colorado School of Mines, Carus Chemical Company, Schumacher Filters of America, Allied Signal Corporation (Kansas City Plant), Millgard Environmental, and Geo-Con.

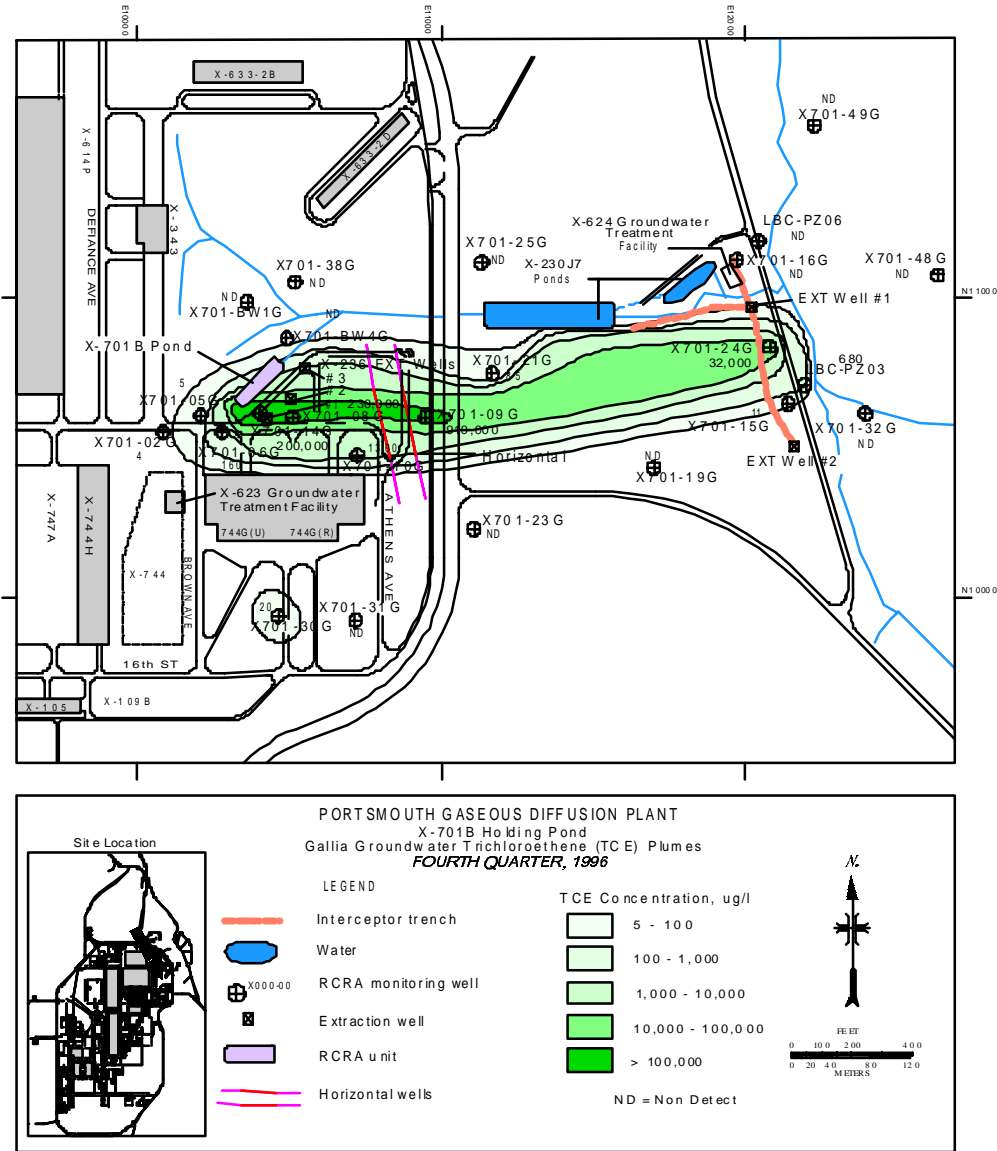


Figure 1. Location of the demonstration site within the X-701B plume at PORTS

- A summary of sites where In Situ Chemical Oxidation Using $KMnO_4$ has been demonstrated as initial treatment for source removal and as full-scale remediations for both DNAPL and BTEX contaminated sites follows:
 - vertical well flushing using $KMnO_4$ at Canadian Forces Base, Borden site ('96);
 - horizontal well-to-well flushing using $KMnO_4$ at the DOE Portsmouth Plant ('96-'98);
 - vertical well flushing and recirculation using $NaMnO_4$ at the DOE Portsmouth Plant ('98); and
 - numerous leaky underground storage tank sites.



- Two overview documents on the use of In Situ Oxidation to treat contaminated ground water are currently in preparation.
 - “Technology Status Review: In Situ Oxidation,” prepared by the U.S. Department of Defense Environmental Security Technology Certification Program. This document, available Dec 1999 (<http://www.estcp.org>), is a brief summary and status of in situ oxidation methods (permanganate, Fenton’s Reagent, and ozone) that have been field demonstrated for source zone treatment.
 - “Guidance for In Situ Chemical Oxidation at Contaminated Sites: An Overview with a Focus on Permanganate-Based Systems,” prepared for the U.S. Department of Energy. This document, available through the PI in winter 1999, 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.

Contacts

Technical

Robert L. Siegrist, Ph.D., P.E.
Colorado School of Mines and Oak Ridge National Laboratory
303-273-3490

Olivia West
Oak Ridge National Laboratory
423-576-5005

Management

Tom Houk
Bechtel Jacobs Company, LLC
Portsmouth Gaseous Diffusion Plant
740-897-6502

James A. Wright
DOE SR, Field Manager, Subsurface Contaminants Focus Area
803-725-5608

All published Innovative Technology Summary Reports are available on the OST Web site at <http://em-50.em.doe.gov> under “Publications.” The Technology Management System, also available through the OST Web site, provides information about OST programs, technologies, and problems. The OST Reference # for In Situ Chemical Oxidation Using KMnO_4 is 167.

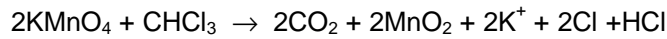


SECTION 2

TECHNOLOGY DESCRIPTION

Overall Process Definition

- The following equation describes the overall chemical reaction for the oxidation of TCE using KMnO_4 :



Stoichiometrically, a ratio of 2:1 oxidant to TCE is required for the chemical reaction.

- Laboratory-scale experiments performed to date have demonstrated that KMnO_4 and hydrogen peroxide (H_2O_2), if applied at sufficient loadings, can effectively oxidize TCE and PCE. Laboratory studies indicate that the reaction is optimized at a 5:1 ratio of oxidant to TCE.
- Oxidation using KMnO_4 involves cleavage of carbon-carbon bonds often facilitated by free-radical oxidation mechanisms. By-products from the reaction include carbon dioxide, manganese dioxide solids, potassium and chloride (when halogenated compounds are oxidized); these by-products are non-toxic at the levels produced.
- Delivery and recirculation of the oxidant is applied to saturated permeable media (hydraulic conductivity $>10^{-4}$ centimeters per second [cm/s]).
- The impacts of natural organic matter that will consume oxidant can be significant and must be considered during the technology selection process at a specific site.

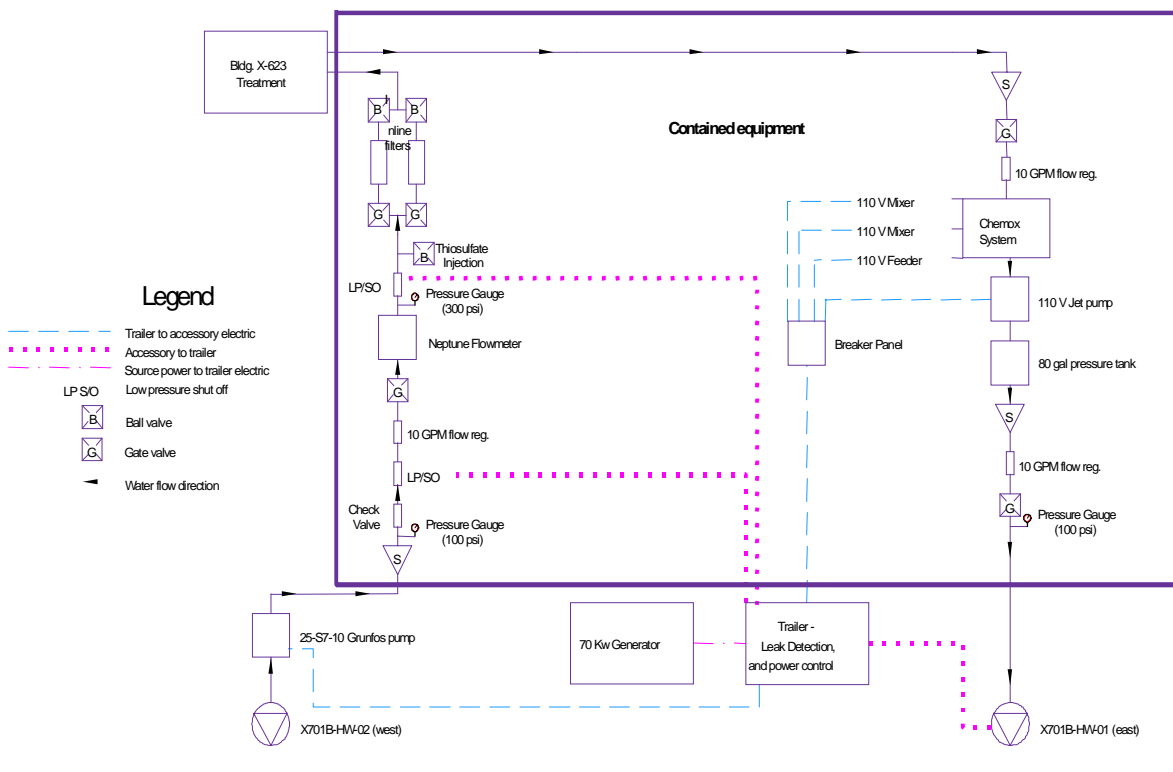


Figure 2. Schematic of In Situ Chemical Oxidation Using KMnO_4 field demonstration site layout



System Design

- The In Situ Chemical Oxidation Using KMnO_4 field demonstration at PORTS was implemented using a pair of horizontal wells, which had been installed with innovative porous polyethylene materials (500 micron) instead of conventional well screens and which transect an area (approximately 90 ft by 200 ft) of DNAPL contamination within the water-bearing unit (Gallia).
- Groundwater was extracted from the west (upgradient) horizontal well to establish hydraulic control, dosed with crystalline KMnO_4 at the surface, and re-injected into the east (downgradient) horizontal well (Figure 2). Prior to oxidant dosing and re-injection, the groundwater was routed to the nearby groundwater treatment facility to ensure compliance with the 5 micrograms per liter (ug/l) TCE injection limit.
- Oxidant dosing consisted of:
 - using a solids feeder (a hopper and auger system) set to deliver a specified amount of crystalline KMnO_4 into a mix tank;
 - gravity flow of the oxidant-laden water into a second mixing tank; and
 - delivery of the oxidant-laden water with a jet pump into the downgradient horizontal well.
- Extraction from the west horizontal well was initially set at ~10 gallons per minute (gpm) by flow regulators, but the formation surrounding the injection well would not accept greater than 6 gpm so the recirculation rate was reduced.
- The recirculation system was designed to operate continuously throughout the duration of the test. It was contained and configured with water-level sensors, low-pressure detectors, and breakers, which would shut down the system automatically should leaks occur. During the demonstration, the system was shut down during the following events:
 - non-routine shut-downs of the groundwater treatment facility;
 - back-up of water within the injection well due to either heavy rainfall or well-screen clogging;
 - heavy rainfall, which tripped the leak detectors; and
 - for repairs to system components.



SECTION 3

PERFORMANCE

Demonstration Plan

- The objectives of the In Situ Chemical Oxidation Using KMnO_4 demonstration were to:
 - evaluate In Situ Chemical Oxidation Using KMnO_4 as a means for delivering oxidants to saturated, permeable subsurface materials;
 - assess In Situ Chemical Oxidation Using KMnO_4 performance in degrading DNAPLs within an aquifer; and
 - obtain cost information for future applications across the DOE complex.
- This demonstration involved treating a portion (90 ft by 220 ft by 6 ft) of the PORTS X-701B DNAPL plume over approximately 30 days.
 - DNAPL compounds (primarily TCE) are located at approximately 25 to 35 ft below ground surface (bgs) at the demonstration site (approximately 12 ft below the top of the water table).
 - The treatment zone consisted of a 119,000 cubic feet (ft^3) ($3,370^3$) volume of soil containing approximately 272.7 pounds (lbs) (123.8 kilograms [kgs]) of TCE.

Demonstration Site Overview

- The X-701B site consists of two unconsolidated units overlying bedrock: the Minford silt and clay and the Gallia sand and gravel. The primary water bearing unit at PORTS is the Gallia, which has a thickness varying from 5 to 6 ft within the region between the horizontal wells at a depth of approximately 27 to 30 ft (bedrock is located at ~35 ft bgs). Groundwater movement within the X-701B area is generally from west to east. Variations from this overall trend are due to surface recharge/drainage features and on-going pump-and-treat activities to control off-site contaminant migration. A more detailed description of the site is included in Appendix B.
- Prior to In Situ Chemical Oxidation Using KMnO_4 , the site was characterized and monitoring locations were established:
 - 22 boreholes were drilled to bedrock (~35 ft bgs);
 - soil samples were collected at 1-ft intervals through the saturated zone (20 to 35 ft bgs, see Appendix B) and analyzed for VOCs; and
 - 3/4-inch PVC wells were installed at 14 of the 22 borehole locations.
- Pre-demonstration TCE concentrations in core samples averaged 53,600 micrograms per kilogram (ug/kg) in the Gallia (the targeted saturated treatment zone), ~19,500 ug/kg in the overlying less permeable Minford, and up to ~132,400 ug/kg in the underlying weathered bedrock (< 6 inches thick) (Table 1). TCE concentrations in the groundwater ranged from below detection limits to ~820,000 micrograms per liter (ug/l) with an average TCE concentration of ~176,700 ug/l

Table 1. Statistical parameters of TCE concentrations in cores collected during the In Situ Chemical Oxidation Using KMnO_4 pretreatment characterization

| Layer | No. of Samples | TCE in Cores (ug/kg)** | | | | |
|-----------|----------------|------------------------|-----------|--------|---------|-----------|
| | | Average | Std. Dev. | Median | Minimum | Max |
| Minford * | 90 | 19,493 | 21,770 | 10,002 | nd | 80,471 |
| Gallia | 163 | 53,596 | 52,713 | 43,320 | nd | 302,237 |
| Sunbury | 13 | 132,405 | 269,791 | 46,932 | 32 | 1,048,174 |

* Based on samples collected at depths > 20 ft.

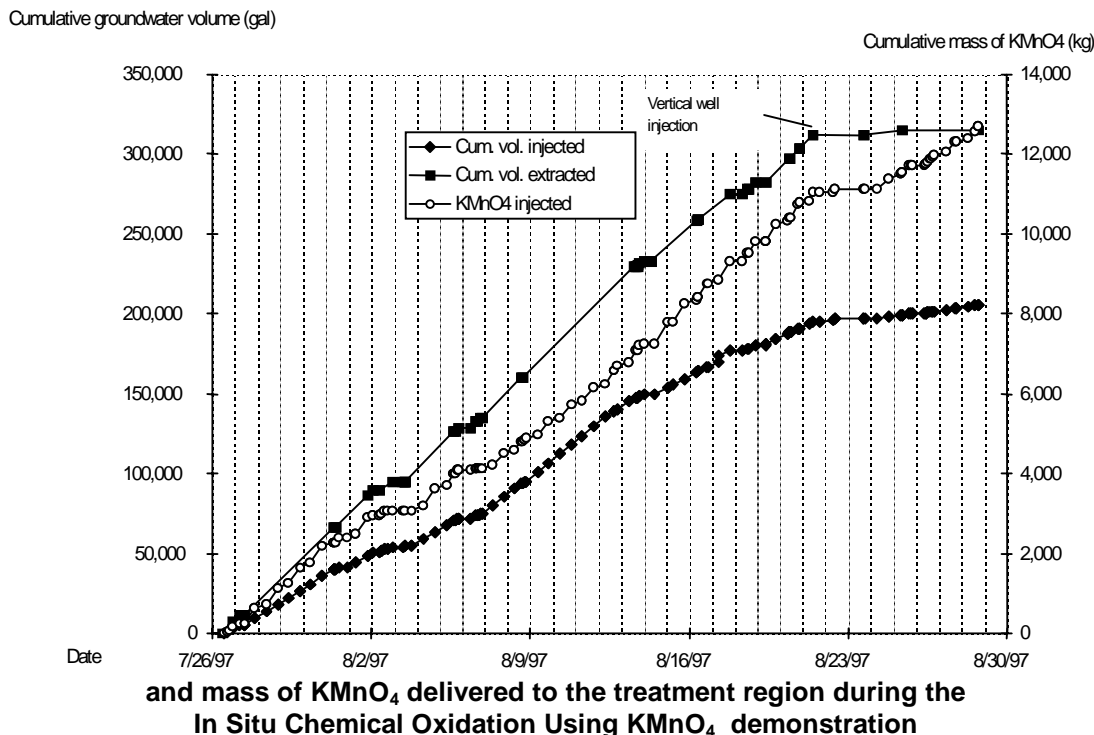
** Based on wet soil weights, nd = not detected at an approximate detection limit of 5 ug/kg.



Operational Description

- Following pre-demonstration characterization, a shakedown test was conducted to identify any potential problems associated with injecting high concentrations of oxidant solution. The test consisted of injecting 500 gallons (gals) of 2% KMnO_4 through a vertical well (75G) [Figure 4]. No problems were encountered.
- The solids feeder (see Figure 2) was set to deliver crystalline KMnO_4 at a rate that would result in a concentration of ~1.5% KMnO_4 at a 10 gpm recirculation rate. Due to the lower flow rate at the groundwater treatment facility (8.5 gpm) and injection well, the initial oxidant concentration was nearly 2.5%. The solids feeder rate was reduced at night to allow continuous injection while the system was unmanned.
- KMnO_4 was recirculated through the horizontal wells for ~27 days. Injection and extraction between the horizontal wells was terminated after 29 days due to increasing amounts of colloidal particulates (amorphous MnO_2 solids, 1um in size), which the groundwater treatment facility was not prepared to handle (plugging of the carbon filters). Subsequent injection of KMnO_4 into a nearby vertical well (74G) was conducted for 8 days to enhance uniform delivery of the oxidant in the region between the horizontal wells.
- A total of 206,000 gals of oxidant solution (~12,700 kilograms [kg] of KMnO_4) was injected into the treatment region. Figure 3 summarizes the cumulative recirculated volume and delivered oxidant mass.
 - ~192,000 gals (~10,700 kg of KMnO_4) delivered into the horizontal well, and
 - ~14,000 gals (~1,900 kgs of KMnO_4) delivered into the vertical well.
- Operation and maintenance of the field equipment during the demonstration included routine monitoring of flow rates, system pressures, oxidant delivery concentrations, and oxidant supply.

Figure 3. Cumulative groundwater injection and extraction volumes



Results

- Delivery of the oxidant solution into the formation through the injection well, i.e. the east horizontal well, was not uniform throughout the length of the treatment region.
 - By day 7, the permanganate had migrated laterally to half-way between the two horizontal wells near the injection point. Yet the permanganate had migrated through the horizontal wellbore only half of the length of the horizontal well screen (it remained undetected near the horizontal well furthest from the point of injection) (Figure 4).

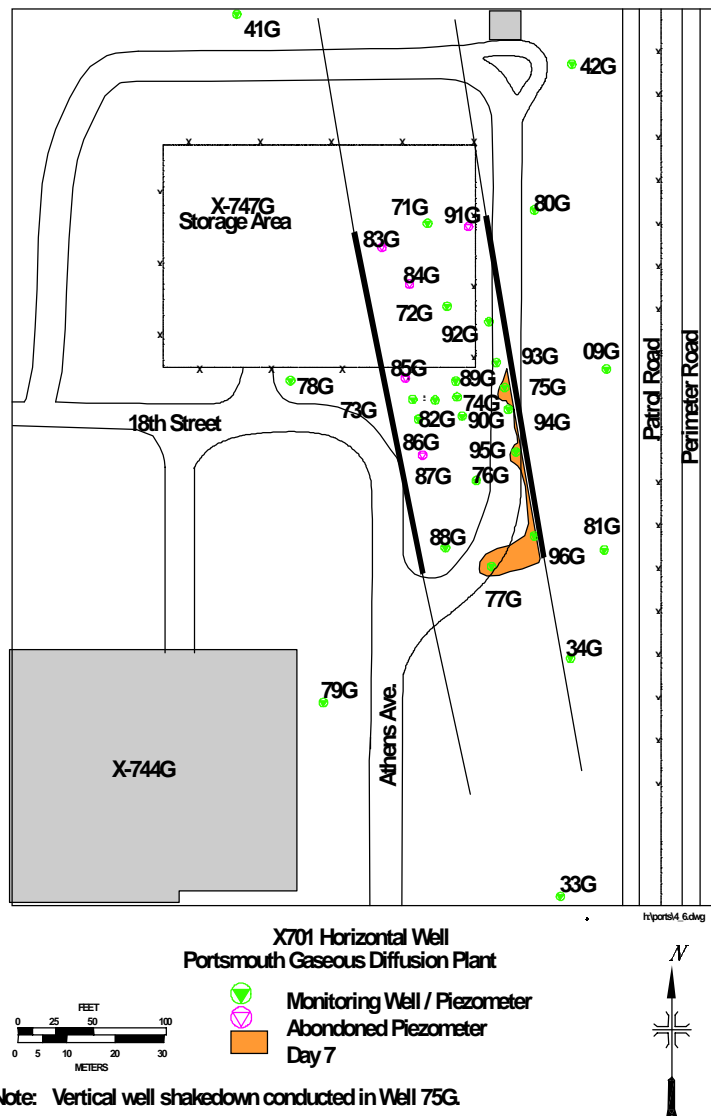


Figure 4. Approximate KMnO_4 distribution 7 days after the In Situ Chemical Oxidation Using KMnO_4 demonstration was initiated

- By day 14, the KMnO_4 had been detected along the entire length of the injection well and in the monitoring well located closest to the extraction well at the end nearest the injection point (84G). However, oxidant detected near the central section of the injection well was attributed to a vertical well shakedown test in well 75G conducted prior to recirculation (Figure 5).

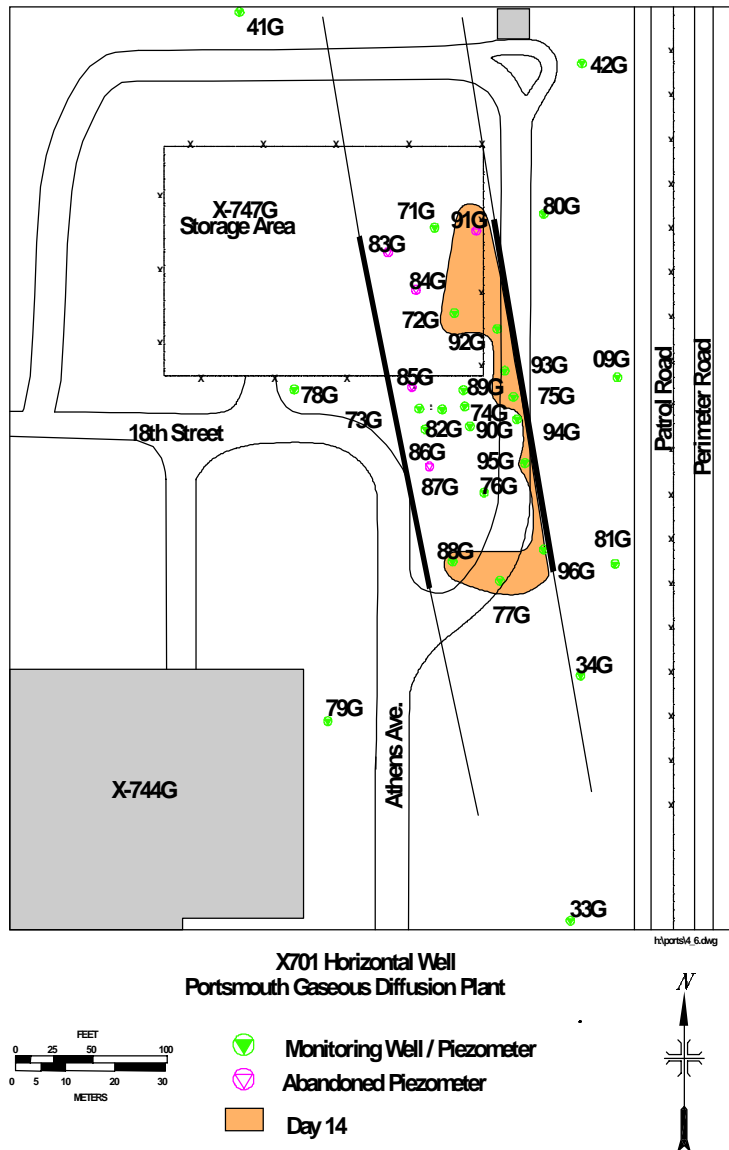


Figure 5. Approximate KMnO_4 distribution 14 days after the In Situ Chemical Oxidation Using KMnO_4 demonstration was initiated

- By day 21, the KMnO_4 had been detected in all monitoring wells within 15 ft of the injection well except near the central section of the treatment zone. Disappearance of the oxidant near the vertical well shakedown test in well 75G indicated that previous oxidant detection was likely due to this test (Figure 6).

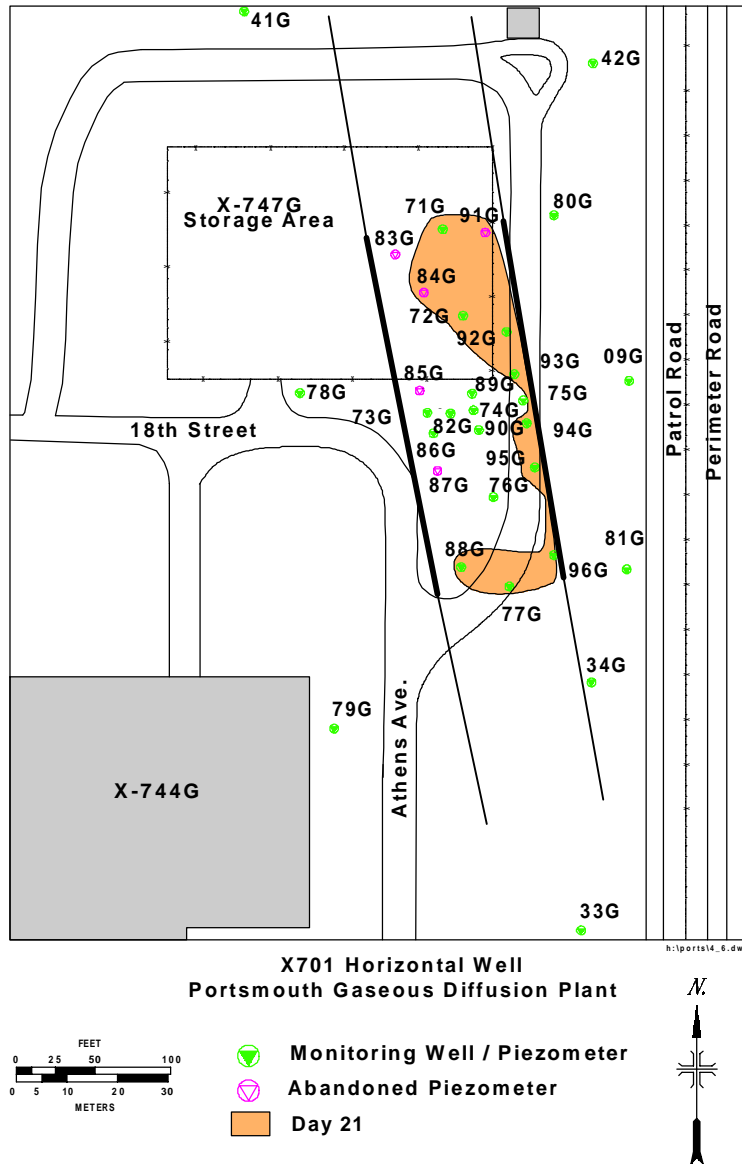
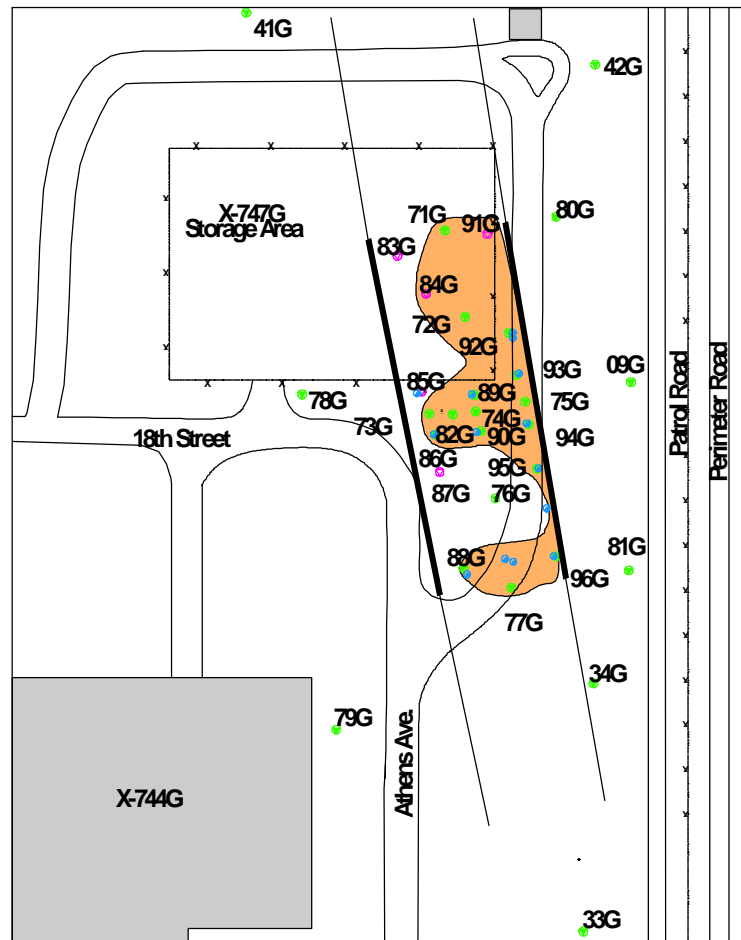


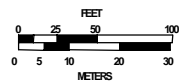
Figure 6. Approximate KMnO_4 distribution 21 days after the In Situ Chemical Oxidation Using KMnO_4 demonstration was initiated

— By day 32, the KMnO_4 was detected in the central monitoring wells but only after oxidant was injected into two vertical wells (73G and 74G) in the area beginning on day 25 (Figure 7).





X701 Horizontal Well
Portsmouth Gaseous Diffusion Plant



- Monitoring Well / Piezometer
- Abandoned Piezometer
- Post-treatment Soil Boring
- Day 32



Note: 73G and 74G vertical well additions started 08/20/97 (day 25)

Figure 7. Approximate KMnO_4 distribution 32 days after the In Situ Chemical Oxidation Using KMnO_4 demonstration was initiated

- Reasons for the non-uniform flow throughout the treatment zone include:
 - heterogeneous conductivities between the horizontal wells (i.e., preferential flow paths due to variable hydrogeologic conditions or the presence of DNAPL within the pore space),
 - potential plugging of the horizontal well screen in the mid-section, and/or
 - insufficient pressures to deliver the oxidant throughout the entire length of the screen.

- Geophysical monitoring was conducted within the demonstration area to track the KMnO_4 injection using DC resistivity. The addition of KMnO_4 increased the fluid conductivity of the groundwater from ~339 to 7250 milli-Siemens per meter (mS/m) (decreased the electrical resistivity from 29 to 1.4 ohm-meter). Field measurements obtained using a multi-electrode resistivity system along two lines indicated subtle changes in the resistivity that correlated with KMnO_4 distribution as detected in monitoring wells and indicated that the KMnO_4 followed preferential flow paths in the Gallia. These preferential flow paths were in agreement with tracer tests conducted in the area after the horizontal wells were installed. Preferential flow paths were created due to heterogeneities in the Gallia and possible clogging of pores by DNAPL. Thus, the progress of the injection front was not uniform. The DC resistivity system was demonstrated to be a useful monitoring tool to map the progress of the oxidation front.
- Pumping tests and bromide tracer tests conducted at the demonstration site after the horizontal wells were installed, but before oxidant introduction, indicated heterogeneous conditions with permeabilities ranging from 40 to 400 feet/day (Korte et al., 1997).
- Immediately after recirculation was terminated, TCE concentrations in groundwater were reduced to very low levels (below detection limits to low ug/l range, Table 2) at those locations where permanganate was detected in the monitoring well.
- Approximately two weeks after the demonstration, post-treatment characterization indicated that soil TCE concentrations had been reduced through the targeted saturated permeable zone (Gallia), but remained near pre-treatment levels in the less permeable zones above (Minford) and below (Sunbury) the targeted zone.
- Estimated average TCE groundwater concentrations in the treatment area were 176 milligram per liter (mg/l) before treatment, 110 mg/l at completion of treatment, and 41 mg/l two weeks after recirculation. Continued groundwater sample collection indicated that estimated average TCE concentrations began to gradually increase to 65 mg/l and 103 mg/l at 8 and 12 weeks after recirculation respectively.
- The continued decline in TCE concentrations within the treatment region after oxidant recirculation was terminated is an indication of continued oxidation of the TCE by the residual permanganate in the treatment region. The gradual increase in TCE concentrations may be attributed to TCE advecting into the area or diffusing out from finer grained, less permeable regions.
- Approximately 10 months after the In Situ Chemical Oxidation Using KMnO_4 demonstration, measurable KMnO_4 residual concentrations were detected at nine locations (although at significantly reduced levels). The persistence of the oxidant solution continued to provide oxidative conditions as indicated by continued low TCE concentrations in the groundwater. At two locations, KMnO_4 had not been observed until completion of recirculation indicating downgradient oxidant migration and oxidation.
- The colloidal material detected after oxidant injection is being analyzed to determine the speciation of the manganese (MnO_4^- , MnO_2 , Mn^{2+} , elemental Mn, etc.) in order to assess any potential adverse toxicity effects down gradient.



Table 2. Summary of TCE concentrations in monitoring wells before, immediately after, and two weeks after the end of the In Situ Chemical Oxidation Using KMnO₄ field demonstration

| Well No. | TCE concentration (ug/l)* | | |
|----------|---|--|--|
| | 7/18/97 Pre-In Situ Chemical Oxidation Using Potassium Permanganate | 8/28/97 Immediately after In Situ Chemical Oxidation Using Potassium Permanganate | 9/13/97 Two weeks after In Situ Chemical Oxidation Using Potassium Permanganate |
| 09G | 250,948 | 582,566 | 147,934 |
| 21G | 862 | 4,792 | 3,059 |
| 41G | 38 | NA | 190 |
| 42G | 0 | 406 | 336 |
| 71G | 28 | 4,820 | 1,706 |
| 72G | 67,645 | ND | 111 |
| 73G | 328,924 | ND | 39 |
| 74G | 733,527 | NA | NA |
| 75G | 176,998 | ND | 83 |
| 76G | 110,220 | 273,849 | 106,080 |
| 77G | 586 | ND | 50 |
| 78G | 820,602 | 797,746 | 339,451 |
| 83G | 3,931 | 5,555 | NA |
| 84G | 45,275 | 7,734 | NA |
| 85G | 774,541 | 692,813 | 179,480 |
| 86G | 224,119 | 7 | 32 |
| 87G | 168,933 | 262,911 | NA |
| 88G | 10,351 | 11 | 46 |
| 89G | 142,736 | ND | 230 |
| 90G | 249,461 | ND | 426 |
| 91G | 6,051 | ND | NA |
| 92G | 14,234 | ND | NA |
| 93G | 129,445 | ND | 125 |
| 94G | 176,908 | ND | 318 |
| 95G | 148,529 | ND | 72 |
| 96G | 1,416 | ND | NA |

*NA = not analyzed; ND = not detected at an approximate detection limit of 5 ppb.



SECTION 4

TECHNOLOGY APPLICABILITY AND ALTERNATIVES

Competing Technologies

- Pump and treat (air stripping) is considered the baseline technology for DNAPL-contaminated groundwater in source zones.
- Other innovative technologies with potential application for source-zone groundwater treatment include:
 - enhancements to pump and treat technologies such as pulsed pumping or high vacuum extraction;
 - in situ air sparging;
 - reactive barrier walls;
 - in situ application of other oxidation processes (e.g., ozone, Fenton's reagent), biological degradation, and chemical degradation;
 - Surfactant/cosolvent flushing; and
 - Thermal treatment (such as steam or electrical heating),
- In Situ Chemical Oxidation Using KMnO_4 has advantages over pump and treat technology at selected sites because it can significantly reduce the time required for remediation, thus lowering operating and maintenance costs over the life cycle of the project.
- In Situ Chemical Oxidation Using KMnO_4 can be used at sites where reactive barriers cannot be applied (e.g. at sites with deep contamination) because the hydrologic conditions and distribution of contaminants at the site preclude the installation of a reactive barrier.
- In Situ Chemical Oxidation Using KMnO_4 is a more aggressive remediation technology than in situ air sparging or bioremediation. Its application at many sites should result in a faster cleanup, thus reducing life-cycle remediation costs for the site.
- In Situ Chemical Oxidation Using KMnO_4 has advantages over other oxidation technologies.
 - It is generally found to result in higher degradation of TCE and PCE under a wider range of conditions when compared to H_2O_2 ,
 - It is inherently more stable than H_2O_2 , which tends to decompose rapidly to H_2O and O_2 when contacted with soil, and
 - It is effective for application where oxidizing power must be maintained over longer time periods, such as when the oxidant needs to access large volumes of subsurface media.
 - It does not require pH adjustment to low pH (e.g. Fenton's reagent).

Technology Applicability

- In Situ Chemical Oxidation Using KMnO_4 can be designed to treat a range of organic contaminants (chlorinated solvents and semi-volatile organics) in soil and groundwater. Operational benefits of In Situ Chemical Oxidation Using KMnO_4 include:
 - rapid reaction kinetics (<10 minutes) with high treatment efficiencies (1.5% KMnO_4 reduced 1000 mg/l TCE to <10 mg/l within 90 minutes);



- applicability to bio-recalcitrant organics;
 - easily coupled with other treatment systems; and
 - flexible and simple (e.g., tailored systems from available components).
- Contaminants oxidizable by permanganates include:
 - Organics: alkenes, aromatics, PAH's, phenols, pesticides, organic acids;
 - Inorganics and metals (e.g., cyanide and iron).
 - In Situ Chemical Oxidation Using KMnO_4 is applicable for in situ destruction of DNAPL or dissolved organic compounds in saturated permeable zones with:
 - hydraulic conductivity greater than 10^{-4} cm/s;
 - low organic carbon (<0.5%);
 - pH >3 and <10 (optimum range is 7 to 8).
 - Depth is a contributor to the overall costs due to implementation of the oxidant delivery (i.e., vertical or horizontal well installation). Other factors contributing to the decision to use this technology include:
 - duration of treatment; and
 - volume/mass of DNAPL to be treated.
 - Potential limitations of In Situ Chemical Oxidation Using KMnO_4 are:
 - it is not as effective as alternative technologies at sites containing saturated organic compounds (e.g., TCA);
 - it is not as effective as alternative technologies at sites containing media with a high natural oxidant demand;
 - there is potential for process-induced detrimental effects (loss of permeability due to particulate MnO_2);
 - redox-sensitive metals may potentially be mobilized under highly oxidizing conditions. However, a demonstration of Fenton's reagent at SRS showed that metals mobilized were below the levels of concern.
 - Benefits of In Situ Chemical Oxidation Using KMnO_4 include:
 - in situ application reduces exposure of workers, minimizes impacts due to site constraints, and typically costs less;
 - the reagent (KMnO_4) is readily available, inexpensive, and results in generation of innocuous materials such as carbon dioxide, manganese dioxide solids, potassium and chloride (when treating chlorinated compounds);
 - the chemistry of the process is well known and has been widely used in wastewater treatment applications;
 - the process is easily applied and controlled;
 - the treatment times and reaction times are rapid; and
 - there is no secondary waste steam produced and the degree of treatment can be regulated and easily combined with other processes.



SECTION 5

COST

Methodology

- Cost information is first presented based on real data from the In Situ Chemical Oxidation Using KMnO_4 demonstration conducted at PORTS in 1997 (Table 3). Demonstration costs were categorized into one of five activities: project management, pre-demonstration characterization, recirculation operations, resistivity monitoring, and post-demonstration characterization.
- Estimated costs are then presented for cleanup of the central portion of the X-701B plume at PORTS using In Situ Chemical Oxidation Using KMnO_4 for the entire life-cycle of the project (Table 4). Assumptions include:
 - In Situ Chemical Oxidation Using KMnO_4 would treat the hot spot, which represents a region 730 ft x 60 ft in size (approximately 998,200 sq. ft or 22.9 acres) and contains at least 90% of the TCE present in the plume;
 - the existing X-624 groundwater treatment facility, down gradient of the X-701B plume, will be used to treat the remaining 10% of the TCE in the plume through continued pump and treat operations;
 - a discounted rate of 4.5% at the “present” year of 1998 is used for calculations;
 - In Situ Chemical Oxidation Using KMnO_4 treatment operations will be conducted for a 6-month period and oxidant will be added to extracted groundwater and then recirculated to minimize disposal costs.
 - the pump and treat system will continue operations as follows:
 - two groundwater treatment facilities are currently being used to treat the X-701B plume water; construction cost of one pump and treat (P&T) facility and the associated operational costs are included; and
 - TCE removal rates and O&M costs (including maintenance, labor, materials, etc) will not change in outlying years.
- A cost comparison to the baseline pump and treat is presented last (Table 5). A cost-effectiveness analysis was prepared specifically for the X-701B site using the P&T facilities at PORTS as the baseline technology for comparison. The X-623 and X-624 groundwater treatment facilities have been operating for several years; thus, cost and performance data are available for these facilities. The cost effectiveness analysis:
 - represents the best estimate of the life-cycle cost to implement In Situ Chemical Oxidation Using KMnO_4 ;
 - does not include the R&D costs for the technology; otherwise, the R&D costs of the baseline technology would also have to be taken into account (DOE, 1997); and
 - includes capital and installation costs for both technologies.
- Labor costs for all three cost analyses assume DOE national laboratory/contractor rates, which are generally higher than consultant rates at industrial sites. O & M rates assume two full-time technical staff, which was utilized for the demonstration but would not be necessary for a full-scale remediation.
- Treatment via chemical oxidation is rapid and most cost effective when used to treat small, highly contaminated zones such as known DNAPL regions or zones of high residual contamination. Thus, three different TCE mass scenarios (8,000, 16,000, and 25,000 lbs of TCE) were evaluated. In each scenario, In Situ Chemical Oxidation Using KMnO_4 was only applied to the portion of the plume with the greatest TCE concentrations (the “hot spot” zone).



Cost Analysis

- Cost for the PORTS In Situ Chemical Oxidation Using KMnO_4 demonstration (including EM50 and EM40 funding) was approximately \$562K. As shown below (Table 3), the majority of the costs relate to the operation of the recirculation system and pre-demonstration characterization.

Table 3. Costs for the PORTS In Situ Chemical Oxidation Using KMnO_4 demonstration

| Demonstration Activity | Estimated Demonstration Cost |
|--|------------------------------|
| Project Management | \$67,440 |
| Pre-demonstration Characterization | \$162,980 |
| Remediation Operations/Oxidant Recirculation | \$162,980 |
| Resistivity Monitoring | \$67,440 |
| Post-demonstration Characterization and Demobilization | \$101,160 |
| TOTAL | \$562,000 |

- Demonstration costs include:
 - generator and oxidant feed system rental accounted for approximately 2% (~\$11,240);
 - other materials (well materials, sampling supplies, etc.) accounted for approximately 6% (~\$33,720);
 - KMnO_4 accounted for approximately 7% (~\$39,340);
 - Travel accounted for approximately 10% (~\$56,200);
 - PORTS site support (health physics, health and safety, construction engineering, waste management, etc.) accounted for approximately 18% (~\$101,160); and
 - Technical support accounted for approximately 53% (~\$297,860).

Estimated costs for the cleanup of the central portion of the X-701B plume containing the highest concentrations and an estimated 90% of the TCE mass are presented in Table 4. Assumptions include: an unburdened labor rate of \$50/hr; O&M labor of 1 staff, 4 hours per day; an oxidant dosing rate of 1.5%; a treatment volume of 730 feet by 60 feet by 5 feet (811 cubic yards). The estimate does not include the cost of well installation.

- Unit costs for the full-scale treatment at the X-701B site are estimated at \$64/cubic yard.

Table 4. Full-scale treatment cost estimate for X-701B site (FY 1998 dollars)

| | |
|---|------------------|
| Engineering Design and Construction Cost: | |
| Includes: treatment design, plan preparation and documentation; 3 to 4 oxidant feed systems, and pumps, piping, etc for the recirculation system. | \$185,000 |
| Pre-Treatment Characterization Cost: | |
| Includes: labor, materials/supplies and sample analysis for 18 borings per acre and 10 samples per boring. | \$99,207 |
| O&M Cost: | |
| Includes: oxidant, generator rental, and labor for system maintenance and monitoring | \$216,935 |
| Post Treatment Monitoring Cost: | |
| Includes: labor, materials/supplies and sample analysis for 9 borings per acre and 10 samples per boring. | \$44,717 |
| Demobilization | \$15,500 |
| Total Estimate (planning level) | \$516,360 |



- A cost comparison of In Situ Chemical Oxidation Using KMnO_4 for three different TCE mass scenarios versus pump and treat at the PORTS X-701B site is presented in Table 5. The costs derived for In Situ Chemical Oxidation Using KMnO_4 conservatively include the capital installation costs and O&M costs to continue operating the X-624 facility to treat the low-concentration, dissolved portion of the plume (10% of the estimated mass). Depending upon regulatory acceptance and many other drivers (e.g., risk reduction analyses, etc.), use of such a P&T facility may not be considered necessary. Such a decision would significantly increase the unit cost savings at this site.

Table 5. Unit costs derived for each TCE mass scenario

| Scenario | TCE Mass ¹ | P&T Cost ² (per lb. TCE treated) | Oxidation Unit Cost ^{2,3} (per lb. TCE treated) | Unit Cost Savings (per lb. TCE treated) |
|----------|-----------------------|--|---|--|
| 1 | 8,000 lbs | \$2,360 | \$778 | \$1,582 |
| 2 | 16,000 lbs | \$1,668 | \$451 | \$1,217 |
| 3 | 25,000 lbs | \$1,318 | \$363 | \$955 |

¹At present year (FY1998)

²All Values in FY1998 Dollars, Assumed Discount Rate = 4.5%

³Excludes R&D costs for the technology

- The cumulative cost for In Situ Chemical Oxidation Using KMnO_4 to date is ~\$1.5 Million (\$1.7 Million FY 1998 "Discounted" Dollars). This cost represents research and development work that has been conducted from FY 1994 through FY 1997. The present value of these R&D costs were used to compute the benefit/cost (B/C) ratio. These B/C ratios for each scenario are presented in Table 6.

Table 6. Benefit/Cost Ratios computed for each TCE mass scenario

| Scenario | TCE Mass ¹ | Savings ² | R&D Costs ^{2,3} | B/C Ratio ⁴ |
|----------|-----------------------|----------------------|--------------------------|------------------------|
| 1 | 8,000 lbs | \$ 12.7 Million | \$1.7 Million | 7.6 |
| 2 | 16,000 lbs | \$19.5 Million | \$1.7 Million | 11.7 |
| 3 | 25,000 lbs | \$23.9 Million | \$1.7 Million | 14.4 |

¹At present year (FY1998)

²All Values in FY1998 Dollars, Assumed Discount Rate = 4.5%

³EM50 R&D costs for in situ chemical oxidation

⁴Savings/R&D Costs

Cost Conclusions

- Unit costs for the In Situ Chemical Oxidation Using KMnO_4 demonstration were \$101 per cubic yard of soil, including oxidant costs of \$21/cubic yard and O & M costs of \$80/cubic yard. An estimate to remediate the central portion of the plume containing ~90% of the contaminant mass of the plume is ~\$64/cubic yard.
- As shown in Table 6, B/C ratios increase with increasing mass of TCE per unit volume. In Situ Chemical Oxidation Using KMnO_4 offers greater savings over baseline technologies when used to remediate source areas as opposed to the lower dissolved concentrations throughout the entire plume.
- Unit costs for In Situ Chemical Oxidation Using KMnO_4 range from \$363 to \$778 per pound of TCE treated, based on three different mass scenarios described in the previous subsection.
- Cost savings estimated by using In Situ Chemical Oxidation Using KMnO_4 as opposed to the baseline pump and treat technology range from \$955 to \$1,582 per pound of TCE treated.



SECTION 6

REGULATORY AND POLICY ISSUES

Regulatory Considerations

- Permits required to deploy this technology depend on the specific application and state/federal requirements. Early and continuous discussions with the regulators will encourage more rapid permitting.
 - An Underground Injection Permit (UIC) may be required. For example, Florida, New Jersey, South Carolina, and Tennessee regulators have stated that they would require a UIC.
 - Comprehensive Environmental Recovery, Compensation, and Liability Act (CERCLA) or Resource Conservation and Recovery Act (RCRA) permitting may likely be required. Because In Situ Chemical Oxidation Using Potassium Permanganate was only a demonstration at PORTS, the nine CERCLA criteria were not addressed. However, many of the criteria, such as protection of human health and environment, community acceptance, implementability, short-term effectiveness, and costs are addressed in other sections of this report.
 - At federal facilities, a National Environmental Protection Act (NEPA) review is required.
 - Because In Situ Chemical Oxidation Using KMnO_4 generates no secondary waste streams, no additional regulatory requirements, such as air or NPDES permits, would likely exist.
- A pilot test or treatability study may be required by some states prior to full-scale implementation.

Safety, Risks, Benefits, and Community Reaction

Worker Safety

- Potential worker safety risks include those associated with standard construction operations as well as those associated with work at a contaminated site and with potentially hazardous chemicals.
- The primary risk to workers occurs during handling of the reactive oxidant (e.g., concentrated permanganate solution). The concentrated permanganate solution is a strong oxidizer and is incompatible with combustibles. Care must be taken to avoid spills and to keep the material away from potentially sparking equipment.
- All field personnel must be 40-h Occupational Safety and Health Administration trained as required in 29 Code of Federal Regulations (CFR) 1910.120 for hazardous waste operations.

Community Safety

- The materials injected (KMnO_4) pose no hazard to the community due to their low concentration after dispersal into the soil or groundwater.
- The community is not exposed to harmful by-products as the overall reaction results in generation of carbon dioxide, MnO_2 solids, cations (e.g., potassium), and halides (when chlorinated solvents are present).
- In Situ Chemical Oxidation Using KMnO_4 does not produce release of volatile organic compounds.
- No unusual or significant safety concerns are associated with transport of equipment or other materials associated with this technology.



Environmental Impacts

- Permanganate is safe in the environment due to the low concentration after dispersal into the soil or groundwater.
- There is no significant environmental impact due to the by-products of the reaction: carbon dioxide, MnO_2 solids, cations (e.g., K) and halides (when chlorinated solvents are present).
- In reducing areas of the aquifer, dissolution of the Mn(IV) in MnO_2 solids could promote the subsequent migration of Mn(II).
- Oxidation of the contaminants does not produce volatile organic compounds (due to cleavage of the organic compound).

Socioeconomic Impacts and Community Perception

- In Situ Chemical Oxidation Using KMnO_4 has minimal economic or labor force impacts.
- The general public has limited familiarity with In Situ Chemical Oxidation Using KMnO_4 ; however, the technology can be explained to the public with ease similar to that of wastewater treatment technologies.



SECTION 7

LESSONS LEARNED

Design Issues

- The recirculation concept of introducing permanganate into the subsurface is viable. Oxidant injection without extraction is feasible; however, there is no control in the subsequent movement of the oxidant after its release. Hence, recirculation is likely a preferable mode of operation.
- Lateral heterogeneities impact the delivery of oxidants through the horizontal wells; whereas, vertical heterogeneities impact the delivery of oxidants through vertical wells.
- If a recirculation approach is used to deliver the oxidant to the subsurface, a system for handling precipitated solids may need to be incorporated into the treatment system for higher oxidant dosing rates and higher contaminant concentrations.
- Higher permanganate concentrations provide faster reaction times, significantly greater removal of DNAPL-type contaminants, but less-efficient oxidant use due to the natural oxidant demand of the subsurface.
- Typical treatment ratios for reagent (KMnO_4) to contaminant are greater than 5:1 based on field and laboratory studies. The efficiency of the process increases at higher contaminant concentrations and decreases as target treatment levels become more stringent.
- Organic carbon content may impact treatment because the permanganate is relatively non-selective. However, no significant effect was observed with contaminant levels near 850 mg/l and total organic carbon of 0.1 to 1.3%.
- For in situ groundwater treatment, the number and pattern of injection and extraction wells and monitoring wells must be designed to ensure maximum coverage of the treatment zone. Because the cost is related to depth and amount of DNAPL, the number and spacing of the wells becomes critical.

Implementation Considerations

- A guidance document for the evaluation and design of In Situ Chemical Oxidation Using KMnO_4 will be available through the project investigators in winter 1999 (see Section 1, Demonstration Summary). Key operating parameters are summarized in the Table 7 below.

Table 7. Key operating parameters of In Situ Chemical Oxidation Using KMnO_4

| Key Reagent Parameter | Comment/Condition |
|----------------------------------|--|
| Formation Characteristics: | |
| Soil and groundwater pH | Permanganate is effective over a pH range of 3 to 12 with an optimum near 7. |
| Soil and groundwater Eh | Background redox conditions must be defined to determine potential impacts on speciation and mobility of non-target metals. |
| Soil and groundwater TOC | Ambient TOC can exert a demand on oxidant. Low TOC (<0.5%) is preferred to limit such demand or excess reagent will be required. This will increase costs. |
| Soil and groundwater temperature | Temperature can impact reaction rates. Extremely low temperatures (e.g., < 10°C) slow reaction rates appreciably; so higher temperatures are preferred. |



| | |
|---|---|
| Soil and groundwater alkalinity and ionic strength. | High carbonate alkalinity can impact free radical oxidation by scavenging the free radicals produced and limiting oxidation efficiency. High ionic strength (e.g., by salts) can reduce reaction rates. |
| Contaminant Properties: | |
| Type and concentration | Applicable to unsaturated halocarbons (PCE, TCE, DCE), aromatics (BTEX), and polyaromatic hydrocarbons (phenols, naphthalene). May mobilize some redox sensitive metals in some settings. |
| Presence of co-contaminants | May alter subsurface biogeochemistry and locally mobilize co-contaminants (e.g., redox sensitive metals such as Cr). Manganese oxides may sorb radionuclides. |
| Treatment Process Characteristics: | |
| Delivered oxidant composition | High concentrations may be needed to deliver adequate oxidant mass in a limited volume that is advected in the system. |
| Handling and Safety | Depending on concentrations and form, permanganate is a strong oxidizer and is incompatible with combustibles. Care is required during handling. |
| Reactivity and effects on formation matrix | Permanganates can lead to some matrix plugging due to precipitation of MnO ₂ solids. |

- Chemical oxidation using permanganate is commonly used in waste-water treatment to oxidize organic compounds and is commercially available in two forms, KMnO₄ and NaMnO₄.
- Injection and extraction wells may eventually become clogged from entrained silt, biological growth, mineral precipitates or other factors, but this effect appeared to be minor based on field demonstrations. Well and matrix clogging is expected to be more apparent during applications of oxidant injection/recirculation at higher oxidant concentrations and within areas of suspected DNAPL.
- When considering the applicability of In Situ Chemical Oxidation Using KMnO₄, general considerations include:
 - pH of the system must be between 3 and 10; and
 - the rate of the reaction increases with higher oxidant to contaminant loading rates.
- When implementing In Situ Chemical Oxidation Using KMnO₄, general operation considerations include:
 - treatment area (including thickness of the aquifer);
 - hydraulic conductivity;
 - recirculation capacity (measure of aquifer conductivity and well size);
 - estimated mass of contaminant present;
 - estimated matrix consumption; and
 - oxidant concentration.
- Sufficient oxidant mass should be delivered to oxidize the contaminant of concern to within specified performance goals. Both contaminant levels present and naturally occurring organic carbon within the matrix will contribute to oxidant consumption. The oxidant consumption rate of the matrix must be considered to ensure that adequate oxidant is delivered to the region.
- The delivery rate of the oxidant will be dependent on the selected well size and aquifer properties (i.e., hydraulic conductivity). The recirculation time may be altered to accommodate slower oxidant delivery rates due to smaller diameter wells or zones of lower permeability.



- The oxidant concentration may be varied to accommodate limited recirculation times or less permeable zones. Lower oxidant concentrations may require longer recirculation times and provide less residual oxidation of the area after recirculation. Higher oxidant concentrations will increase treatment cost and may utilize the delivered oxidant less efficiently (residual oxidant will continue to be consumed by the matrix).
- Greater control of oxidant delivery as well as treatment reliability may be achieved with closer well spacings. However, greater costs are associated with closer well spacing due to the additional wells required. Complex sites may require a combination of closely spaced and more widely spaced wells depending upon local heterogeneities. Fractured rock sites may be especially difficult to design a system that ensures uniform delivery of oxidant.
- Implementation of this technology does not require permanent infrastructure such as a permanent power source (temporary power is required), or permanent water and chemical tanks, etc. Temporary power is required for operation of the recirculation system.
- The by-products of in situ chemical oxidation are innocuous. Because treated groundwater is recirculated (i.e., re-injected into the subsurface) no solid or liquid waste is generated from the treatment process other than drilling spoils.

Needs for Future Development

- Natural oxidant demand within a treatment area as related to oxidant dosing requirements needs to be better understood.
- Optimization of the oxidant to contaminant ratio must be further evaluated. While lower oxidant concentrations have been shown to be effective in the field, the residual concentrations may not be sufficient to treat contaminants within lower permeability zones. Higher oxidant concentrations will provide better residual oxidant for diffusion into the lower permeability areas, but may result in less efficient oxidant used (residual oxidant will be consumed by the natural oxidant demand within the matrix).

Technology Selection Considerations

- Depth is a major factor when considering selection of this technology for deployment at a specific site. Other factors contributing to the decision to use this technology include:
 - organic carbon content of the formation;
 - the pH range (alkaline environments may not be suitable or may require pre-treatment to bring the pH into optimum range);
 - volume of DNAPL; and
 - cleanup goals.



APPENDIX A

REFERENCES

- Case, T. 1997. *Reactive permanganate grouts for horizontal permeable barriers and in situ treatment of ground water*. M.S. thesis, Environmental Science & Engineering Division, Colorado School of Mines, Golden, CO.
- Case, T. L. and R. L. Siegrist. 1998. Oxidation Kinetics of Trichloroethylene in Groundwater by Permanganate under Varying Matrix Conditions. *Water Environment Research*, submitted for publication.
- Cline, S. R., West, O. R. et al. 1997. Mixed region chemical oxidation of TCE-contaminated silty clays using potassium permanganate: Laboratory treatability studies and a full-scale field test at the Kansas City Plant. In preparation.
- Gates, D.D. and R.L. Siegrist. 1995. In Situ Chemical Oxidation of Trichloroethylene Using Hydrogen Peroxide. *ASCE Journal of Environmental Engineering* **121**(9): 639-644.
- Gates, D.D., Siegrist, R.L., and S.C. Cline. 1997. Chemical Oxidation of Organics in Soil: 1. Effects of Contaminant and Oxidant Type. *Water Environment Research*. In preparation.
- Korte, N. E., M. Muck, P. M. Kearl, R. L. Siegrist, T. C. Houk, R. M. Schlosser, and J. L. Zutman. 1997. *Field Evaluation of a Horizontal Well Recirculation System for Groundwater Treatment: Field Demonstration at X-701B Portsmouth Gaseous Diffusion Plant, Piketon, Ohio*. Oak Ridge National Laboratory, Grand Junction, CO.
- Siegrist, R. L., M. I. Morris, O. R. West, D. A. Pickering, et al. 1994. *X-231B Technology Demonstration for In Situ Treatment of Contaminated Soil: Field Evaluation of Mixed Region Vapor Stripping, Chemical Oxidation, and Solidification Processes*. ORNL/TM-12261. Oak Ridge National Laboratory, Oak Ridge, Tennessee.
- Siegrist, R. L., K. S. Lowe, L. C. Murdoch, D. A. Pickering, and T. L. Case. 1998a. In Situ Oxidation by Fracture Emplaced Reactive Solids. *J. Environmental Engineering*. Submitted for publication.
- U. S. DOE. 1994a. *Quadrant II RFI Report for Portsmouth Uranium Enrichment Plant, Piketon, Ohio. Volume I (draft)*. U. S. Department of Energy, Office of Environmental Restoration and Waste Management. Piketon, Ohio.
- U. S. DOE. 1994b. *X-701B Draft Cleanup Alternatives Study/Corrective Measures Study Report for the Portsmouth Gaseous Diffusion Plant, Piketon, Ohio*. U. S. Department of Energy, Office of Environmental Restoration and Waste Management. Piketon, Ohio.
- U. S. DOE. 1994c. *X-701B Draft Cleanup Alternatives Study/Corrective Measures Study Report for the Portsmouth Gaseous Diffusion Plant, Piketon, Ohio*. U.S. Department of Energy, Office of Environmental Restoration and Waste Management. Piketon, Ohio.
- U.S. DOE. 1997. *Draft, Cost Savings Deliverables and Criteria for the OST Technology Decision Process*, version 1.4, April 25, 1997.
- West, O.R., S. R. Cline, W. L. Holden, F. G. Gardner, B. M. Schlosser, J. E. Thate, D. A. Pickering, T. C. Houk. 1998. *A Full-scale Demonstration of In Situ Chemical Oxidation through Recirculation at the X-701B Site: Field Operations and TCE Degradation*. ORNL/TM-13556. Oak Ridge National Laboratory, Oak Ridge, Tennessee.
- West, O.R., R.L. Siegrist, J. S. Gierke, et al. 1995. In Situ Mixed Region Vapor Stripping of Low Permeability Media. 1. Laboratory Experiments. *Environ. Science & Technology*. **29**(9):2191-2197.



Feenstra, S., J.A. Cherry, and B.L. Parker. 1996. Conceptual models for the behavior of dense non-aqueous phase liquids (DNAPLs) in the subsurface. *Dense Chlorinated Solvents*, J.F. Pankow and J.A. Cherry, editors, Waterloo Press, Guelph, Ontario, Canada.

Korte, N., L. Liang, B. Gu, M. Muck, J. Zutman, R. Schlosser, R. Siegrist, T. Houk, and Q. Fernando. 1997a. *In Situ Treatment of Mixed Contaminants in Groundwater: Application of Zero-Valence Iron and Palladized Iron for treatment of Groundwater Contaminated with TCE and Tc99*. ORNL/TM-13530. Oak Ridge National Laboratory, Oak Ridge, TN.

Korte, N., M. Muck, P. Kearl, R. Siegrist, T. Houk, R. Schlosser, and J. Zutman. 1997b. *Field Evaluation of a Horizontal Well Recirculation System for Groundwater Treatment: Field Demonstration at X-701B Portsmouth Gaseous Diffusion Plant, Piketon, Ohio*. ORNL/TM-13529. Oak Ridge National Laboratory, Oak Ridge, TN.

Korte, N.E., P.M. Kearl, R.L. Siegrist, M.T. Muck, and R.M. Schlosser. 1999. An Evaluation of Horizontal Recirculation Using Single Well Tests, Pumping Tests, Tracer Tests and the Colloidal Borescope. *Ground Water Monitoring and Review*. In press.

Nyquist, J. E., Carr, B. and, Davis, R. K. 1998. Geophysical monitoring of a demonstration of in situ chemical oxidation: *Proceedings of the 10th Annual Symposium of the Application of Geophysics to Environmental and Engineering Problems, Eng. Environ. Geophys. Soc.*, 583-591.

Nyquist, J.E., B.J. Carr, and R.K. Davis. 1999. DC Resistivity Monitoring of Potassium Permanganate Injected to Oxidize TCE In-Situ. *Journal of Environmental and Engineering Geophysics*. In press (Sept 99).



APPENDIX B

DEMONSTRATION SITE CHARACTERISTICS

Site History/Background

- The Portsmouth Gaseous Diffusion Plant (PORTS) is approximately 80 miles south of Columbus, 20 miles north of Portsmouth, and 1 mile east of U.S. Route 23, near Piketon in south-central Ohio (Fig. B.1). The industrialized portion of PORTS is approximately 1,000 acres of a 3,714-acre DOE reservation. PORTS was constructed between 1952 and 1956 and has operated since January 1955 enriching uranium for electrical power generation. Until 1991, PORTS also provided highly enriched uranium to the U.S. Navy.

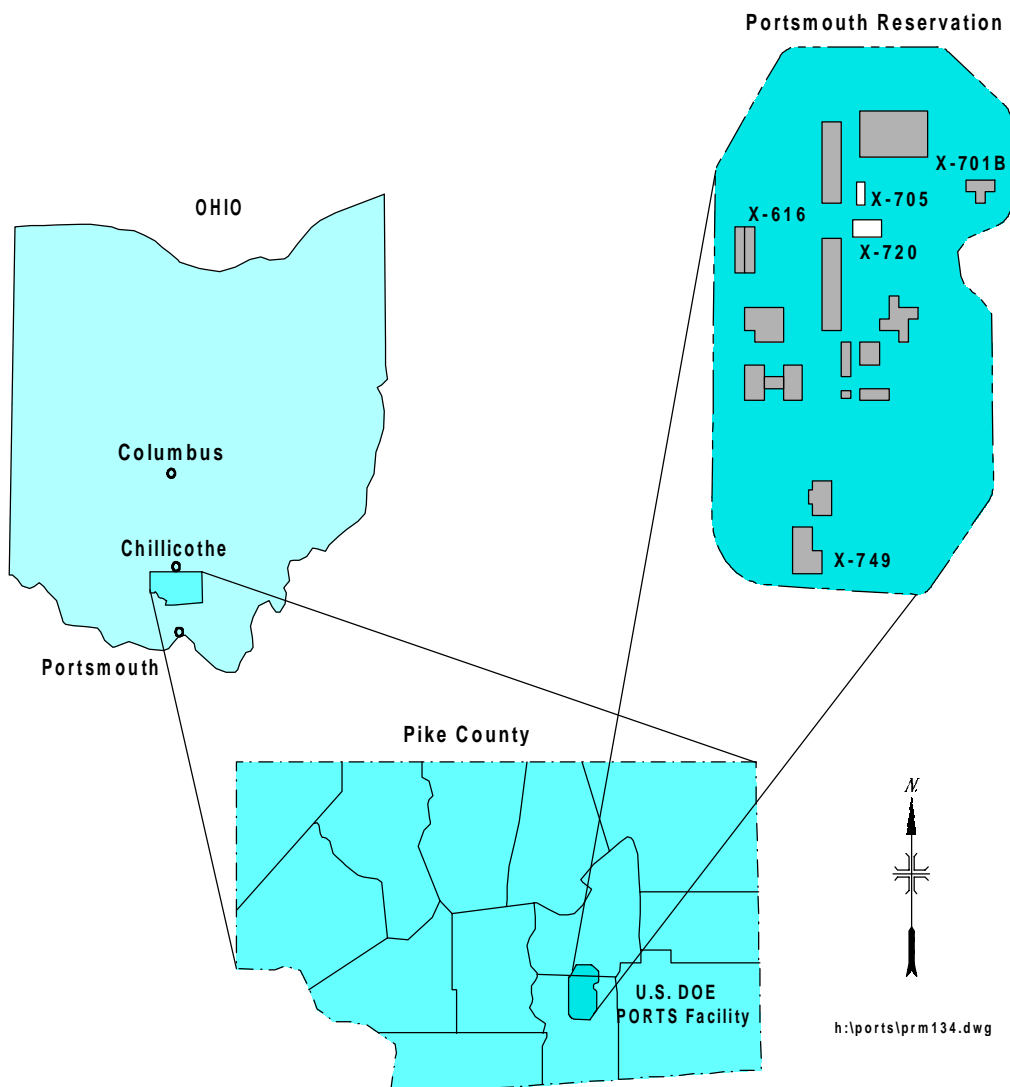


Figure B.1. Location of the Portsmouth Gaseous Diffusion Plant



- The X-701B site, located in the northeastern area of PORTS, contains an unlined holding pond, 200-ft by 50-ft in area. The pond was used from 1954 to 1988 for the neutralization and settling of metal-bearing acidic wastewater and solvent contaminated solutions primarily originating from the X-700 Chemical Cleaning Facility and the X-705 Decontamination Building. From 1974 through 1988, slaked lime was added to the X-701B influent to neutralize its low pH and induce precipitation, which caused large amounts of sludge to accumulate in the pond. The holding pond was drained and the contaminated sludge and underlying silt and clay were removed as part of a RCRA closure action in 1990.

Contaminant Locations and Hydrogeologic Profiles

- The stratigraphy at the X-701B site consists of two unconsolidated units overlying bedrock. A summary of these units is:
 - the Minford silt and clay with a thickness of 25 to 30 ft;
 - the Gallia sand and gravel, which has a thickness varying from 2 to 10 ft (5 to 6 ft within the region between the horizontal wells);
 - the Sunbury shale, the first bedrock layer, consists of 10 to 15 ft of moderately hard shale that often exhibits an upper weathered zone of gray, higher plastic clay; and
 - the Berea sandstone (~15 feet thick) at approximately 47 ft bgs at X-701B.
- A pumping test conducted at the upgradient (west) horizontal well, indicated a hydraulic conductivity of approximately 20 ft/day (7×10^{-3} cm/s). Single-well pump tests conducted on several vertical monitoring wells between the horizontal wells indicated hydraulic conductivities ranging from 24 to 411 ft/day.
- Groundwater movement in the Gallia within the X-701B area is generally from west to east, with variations from this overall trend due to surface recharge/drainage features and on-going pump-and-treat activities to control off-site contaminant migration.
- During the Quadrant II RCRA Facility Investigation, TCE was detected in a groundwater sample from a well near the horizontal wells at a concentration of 700,000 ug/l. The presence of TCE as a DNAPL phase can be inferred from this concentration, which is very close to the solubility limit of TCE in water. DNAPL has been observed in a number of wells within the X-701B area near the holding pond. Technetium has also been detected at an activity of 926 picocuries per liter (pCi/l).
- Migration of the contaminants in the X701B plume to the southwest and discharge to the Little Beaver Creek is currently being controlled by an interceptor trench and extraction wells. Groundwater is pumped from the extraction wells at a rate of ~50 gpm and treated using air strippers and activated carbon at a nearby groundwater treatment facility.



APPENDIX C

DEMONSTRATION PERFORMANCE

Hydraulic Testing

Extensive hydrodynamic testing was performed as part of a program to evaluate horizontal recirculation as a means of removing/treating contaminants in thin, interbedded aquifers (Korte et al. 1997a, 1997b and 1999). Testing was conducted at two PORTS locations, the Clean Test Site and X-701B. Specific to the X-701B site, the following testing was conducted:

- Single well tests (bail and slug tests) at 22 piezometers within the flow field;
- 48-hour pumping tests on each horizontal well to determine well yield, recirculation rate, extent of drawdown, and influence of heterogeneities;
- Evaluation of aquifer heterogeneity through use of a colloidal borescope to observe natural colloidal movement; and
- A bromide tracer test (500 mg/l injected into the downgradient horizontal well after quasi-steady state conditions were established in the flow field).

Key Results

- Single well tests indicated approximately an order of magnitude range of hydraulic conductivities (30 to 410 feet per day (ft/d) or 0.01 to 0.15 cm/s) within the area of interest.
- The pumping tests indicated an average hydraulic conductivity of 20 ft/d or 0.007 cm/s and bromide breakthrough indicated an average linear velocity between horizontal wells of 6.7 ft/d or 0.0024 cm/s.
- Direct observation, with the colloidal borescope, indicated swirling, non-directional flow patterns typical of zones where little or no natural flow is occurring.
- Significant heterogeneities within the flow field were observed during the bromide tracer test:
 - Maximum bromide peak detected in 77G, located 45 ft from the injection well, within 20 hours;
 - Maximum bromide peak detected in 75G, located 15 ft from the injection well, within 200 hours; and
 - Maximum bromide peak detected in 73G and 74G, located ~45 ft and 85 ft respectively from the injection well and within the most contaminated area, at 500 to 750 hours.

Reduced permeability in the central sandy zone at X-701B may be due to the presence of DNAPL. Such an effect is consistent with preferential filling of larger pores with DNAPL (Cohen and Mercer 1993) and that, in a source zone, DNAPL can occupy 40 to 70% of the bulk pore space causing permeability in such zones to be substantially reduced (Feenstra et al. 1996). Therefore, the problem of aquifer heterogeneity may be exaggerated by the presence of DNAPL.

Geophysical Testing

The two principal objectives of the geophysical monitoring were to:

- Confirm that the injection of potassium permanganate can be monitored from the surface using DC resistivity; and
- Determine if DC resistivity provides sufficient resolution to detect preferential flow along the injection front in order to identify which portions of the Gallia aquifer were bypassed during treatment.

Geophysical monitoring was conducted within the ISCOR demonstration area to track the KMnO_4 injection using DC resistivity (Nyquist et al., 1998 and 1999). The monitoring consisted of:

- Preliminary modeling to determine if the geophysical signature could be detectable using surface DC resistivity;
- Collection of background resistivity data prior to recirculation along five lines (Figure C.1), both between the two horizontal wells, and down gradient (east) of the wells;

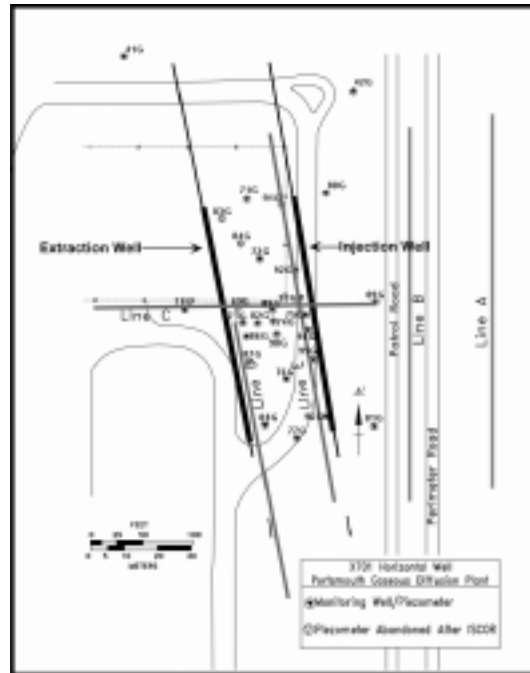


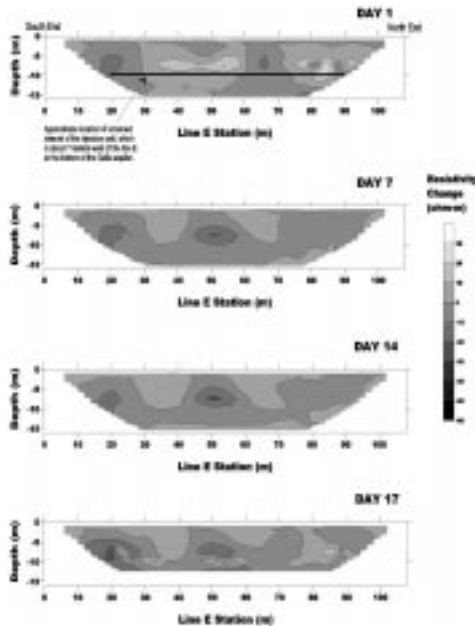
Figure C.1. Location of geophysical monitoring lines

- Collection of field measurements along 2 lines (C and E, Figure C.1) during KMnO_4 recirculation using a Sting/Swift multi-electrode resistivity system that:
 - automatically triggers a series of measurements to collect a full resistivity sounding;
 - uses a uniform electrode spacing; and
 - collects sounding data with 28 electrodes per line in less than an hour.

Key Results

- Despite the strong electrical contrast that would be created by injecting the KMnO_4 solution, resistivity changes in the thin Gallia aquifer were detectable beneath ~15 ft of conductive clay.
- The addition of 1% KMnO_4 increased the fluid conductivity of the groundwater from ~339 to 7250 mS/m (decreased the electrical resistivity from 2.9 to 1.4 ohm-m).
- The background resistivity data for a line parallel to the injection well, line E, indicates that the Gallia aquifer is not uniform, with the maximum resistivity at the south end and in the center with a distinct decrease in resistivity at the north end of the line.

- Field measurements obtained using a multi-electrode resistivity system along two lines indicated subtle changes in the resistivity that correlated with KMnO_4 .
- Both of the high resistivity zones showed a significant decrease in resistivity by day 7 (Figure C.2) and appeared to reach steady state by day 17.



- Evolution of the resistivity from day 1 to day 17 showed that the breakthrough front was heterogeneous, with the majority of the potassium permanganate emerging at the center and at the southern end of the line.
- On Day 21 there is still very little sign of flow near the center of the injection well where line C was located (Figure C.3).

Figure C.2. Resistivity along Line E during recirculation

- The resistivity data indicated non-uniform progression of the KMnO_4 during the demonstration likely due to heterogeneities in the Gallia aquifer, which correlates with the heterogeneity found in the drilling records, during hydraulic testing, and by contaminant monitoring.

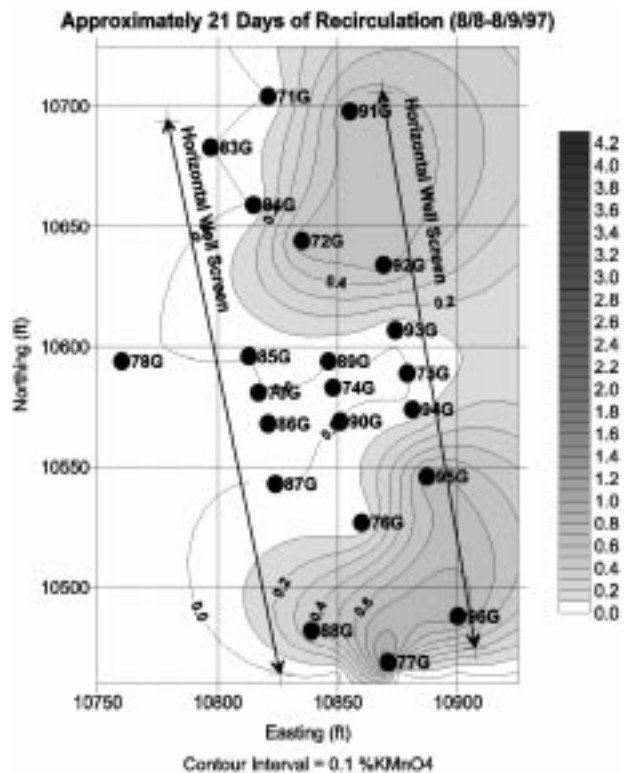


Figure C.3. Distribution of KMnO_4 21 days after recirculation