Appendix A8

OU1 Remedial Work Plan

Day Environmental, Inc.

February 9, 2007

OU1 REMEDIAL WORK PLAN
FORMER AIR FORCE PLANT 51
4777 DEWEY AVENUE, GREECE, NEW YORK
DERP-FUDS SITE NO. C02NY057500
NYSDEC SITE NO. V00421

OPERABLE UNIT OU1
AOC1 (FORMER PLATING POND/LAGOON)

Prepared For: 4800 Dewey Avenue, Inc.
80 Steel Street
Rochester, New York 14606

Prepared By: Day Environmental, Inc.
40 Commercial Street
Rochester, New York 14614

Project No.: 2806S-01

Date: September 29, 2006
Revised Date: February 9, 2007

OU1 REMEDIAL WORK PLAN
FORMER AIR FORCE PLANT 51
4777 DEWEY AVENUE, GREECE, NEW YORK
DERP-FUDS SITE NO. C02NY057500
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OPERABLE UNIT OU1
AOC1 (FORMER PLATING POND/LAGOON)

Date: 2/9/07

Jeffrey A. Danzinger
Project Manager

David D. Day, Pres. Date: 2/9/07

David D. Day, P.E.
President

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Alexander B. Grannis
Commissioner

May 18, 2007

RECEIVED
MAY 22 2007

Mr. Louis Atkin
4800 Dewey Avenue Enterprises, Inc.
80 Steel Street
Rochester, NY 14606

Dear Mr. Atkin:

RE: Voluntary Cleanup Project
Former Air Force Plant 51; Site #V00421-8
Operable Unit 1
OU1 Remedial Work Plan; February 9, 2007

The New York State Department of Environmental Conservation (NYSDEC) has completed its review of the February 9, 2007 OU1 Remedial Work Plan (OU1 RWP) prepared by Day Environmental for the Former Air Force Plant 51 site. Based upon the information and representations given in the OU1 RWP and the April 3, 2006 Environmental Site Investigation Report for Operable Unit 1, the OU1 RWP is hereby approved with the following modifications and clarifications.

1. Alternative drilling procedures will be used if the direct-push equipment is not able to achieve the required depths or is otherwise ineffective.

2. If needed, a contingency remedy to protect public health and/or prevent off-site migration could include additional source control and/or migration control at the perimeter of the site. Additionally, NYSDEC may request development and implementation of a contingency remedy at any time if it is determined that the selected remedy cannot achieve the remedial action objectives established for Operable Unit 1.

3. Section 3.4 Institutional Controls: The requirement to evaluate the potential for vapor intrusion into any building to be constructed on the Site will apply to the entire site (not just the area around Operable Unit 1) and will be included in the environmental easement.

4. Section 4.0: The environmental easement will be completed as soon as possible. The draft easement will be submitted to NYSDEC for review by July 9, 2007.

The OU1 RWP consists of this letter and the February 9, 2007 OU1 Remedial Work Plan prepared by Day Environmental, Inc. Please submit nine (9) CDs containing electronic copies of the OU1 RWP (including this letter) by June 25, 2007. Please ensure that the electronic files are in pdf format and that the text of the report is searchable.

Per the OU1 RWP, the remedial design investigation will start by June 25, 2007. Please notify me when the field work has been scheduled.

Thank you for your cooperation in this matter and please contact me at (585) 226-5357 if you have any questions.

Sincerely,

Frank Sowers, P.E.
Project Manager

cc:
Jeff Danzinger (Day Environmental)
David Day (Day Environmental)
David Freeman, Esq.

ec:
Bart Putzig
Ed Belmore
Joe Hausbeck
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Joe Albert
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EXECUTIVE SUMMARY

This Remedial Work Plan was prepared for the subject property (Site), which consists of an approximate 33.6-acre property (addressed as 4777 Dewey Avenue) located on the west side of Dewey Avenue in the Town of Greece, County of Monroe, New York and is commonly referred to as the former Air Force Plant No. 51 (AFP51). This Remedial Work Plan for Operable Unit OU1 (OU1 Remedial Work Plan) was developed in accordance with the requirements of Voluntary Agreement Index #B8-590-01-02 between the New York State Department of Environmental Conservation (NYSDEC) and 4800 Dewey Avenue, Inc. (4800 Dewey). Operable Unit OU1 is comprised of the following two areas of concern (AOCs):

> **AOC1 Former Plating Pond/Lagoon:** Information indicates that plating rinse wastewater was disposed of into a man-made plating pond/lagoon, which ultimately flowed to Round Pond Creek. Chlorinated volatile organic compounds (VOCs), petroleum-related VOCs, semi-volatile organic compounds (SVOCs), and some metals have been detected in sediment, soil and/or groundwater at, or in proximity to, the former plating pond/lagoon. As an initial remedial action, surface water in the plating pond/lagoon was removed via pumping, and the United States Army Corps of Engineers (USACE) excavated underlying sediments/soils down to the top of the groundwater table in 2000/2001. However, contamination, including dense non-aqueous phase liquid (DNAPL) that predominantly consists of chlorinated VOCs, is still present at AOC1. Under the Voluntary Cleanup Agreement (VCA), the nature and extent of contamination at AOC1 was further delineated, on-going DNAPL monitoring and recovery has been implemented as an interim remedial measure (IRM), and it was determined that further remediation of AOC1 is warranted.
>
> **AOC2 Lagoon and Stormwater Outfalls:** A discharge point associated with the former plating pond/lagoon is located west of Building #1 just outside the fence of the Site (i.e., approximate property line). The USACE remediated soil and sediments in the discharge ditch downstream of the former plating pond/lagoon, but stopped at the property line. Discharges to the former plating pond/lagoon outfall have been eliminated as a result of the USACE's remediation efforts. Since there are no more discharges to the former plating pond/lagoon, and since discharges from the stormwater system are being controlled, further work at AOC2 has not been requested by regulatory agencies.

Site Background

The facilities on the Site were generally constructed in the early 1940's. The Department of Defense either owned or leased facilities situated on approximately 44 acres of land located in the Town of Greece, New York, including the Site. These facilities were used for the manufacture of ocean-going ships and cranes during and immediately following World War II, and subsequently for the manufacture of B-52 aircraft parts and Talos ground handling equipment. 4800 Dewey currently owns the Site.

The Site is currently bounded to the north by the Monroe County Shoremont Water Treatment Plant; to the east by Dewey Avenue, with a residential apartment complex beyond; to the west by vacant undeveloped land and New York State/Federal wetlands (containing Round Pond Creek); and to the south by the Ontario State Parkway with residential property beyond.

Remedial Design Investigation

Under this Remedial Work Plan, a remedial design investigation would initially be performed to further evaluate/define the extent of VOC impact to soil and groundwater on the Site in the area generally between existing monitoring well MW1-7 and the former plating pond/lagoon. Additional goals of the remedial design investigation include obtaining information that can be used for the selection and design of the remedial program for this area, and obtaining information that can be used to fill data gaps, if any. The results of the remedial design investigation will be used to design the remedial actions specified herein with concurrence from the NYSDEC.

The proposed remedial design investigation consists of the advancement of nine test borings, the installation of one groundwater monitoring well at one of the test boring locations, and the collection and analysis of soil samples and groundwater samples. A groundwater potentiometric contour map will also be prepared for this area of the Site.

Remedial Activities

The proposed remedy selected to address contamination at operable unit OU1 area of concern AOC1 (former plating pond/lagoon) consists of the following components:

- In-Situ Chemical Oxidation of the On-Site Source Area
- Post-Treatment O&M Groundwater Monitoring
- Institutional Controls

In-situ chemical oxidation will be conducted in subsurface soils and groundwater in the source area (i.e., generally an approximate 100-foot by 140-foot area within, and around, the former plating pond/lagoon location). A remediation contractor will be retained to perform remediation services using hydrogen peroxide with a site-specific formulated catalyst (Fenton's reagent), and possibly sodium permanganate during a polishing treatment. In-situ chemical oxidation is the process of oxidizing contaminants in the groundwater and soil by injecting water containing high concentrations of an oxidant to the area of contamination. This technology can eliminate (i.e., permanently destroy) many organic contaminants in both saturated and unsaturated environments by changing the organic contaminants into harmless materials, such as water and carbon dioxide.

The chemical oxidation remedial work is divided into a Pilot Phase, a Full-Scale (Primary) Phase, and a Polishing Phase (if deemed necessary). Remedial design plans will be developed and implemented for each phase, and will include: a sampling plan; a health and safety plan; and details concerning injector construction, mixing and application of injectates, process monitoring and performance monitoring. The use of Fenton's reagent and sodium permanganate will be evaluated separately during the Pilot Phase.

The Pilot Phase will be conducted on just a portion of the source area that requires treatment. The Full-Scale Phase and any Polishing Phase are intended to treat the entire source area. In general, the findings of the Pilot Phase treatment using both the Fenton's reagent and the sodium permanganate will be used to confirm the use of these chemical oxidation techniques at AOC1 and assist in development of the remedial design plans for the Full-Scale Phase and Polishing Phase (if deemed necessary). It is currently anticipated that Fenton's reagent would be used during the Full-Scale Phase, and that sodium permanganate would be used during the Polishing Phase (if deemed necessary).

Subsequent to completion of the in-situ chemical oxidation, a post-treatment operation and maintenance (O&M) groundwater monitoring program will be implemented using the AOC1 groundwater monitoring wells that exist at that time in order to evaluate the effectiveness of natural attenuation, the presence and concentration of VOCs, and to determine the extent and potential movement of contamination. This O&M groundwater monitoring will continue for a period of up to five years. Completion of this five-year O&M groundwater monitoring represents a decision point for the remedy. Potential outcomes include closure of the operable unit, further monitoring of the operable unit, additional chemical oxidant injections at the operable unit, or selection and implementation of a contingency remedy.

As part of the remedy, institutional controls will be implemented that include the following elements:

- Development and implementation of a Site Management Plan (SMP) to:
  - Address the characterization, handling, and disposal/re-use of any media (e.g., soil, fill, groundwater) that is disturbed during any future activities at the entire Site;
  - Evaluate the potential for vapor intrusion into any future buildings to be constructed on the Site in the areas of AOC1, including requirements to mitigate such potential vapor intrusions through use of environmental engineering controls or other means;
  - Identify use restrictions for the Site;
  - Include a health and safety plan (HASP) and a community air monitoring plan (CAMP) to assist in reducing potential exposures to Site contaminants.
  - Include an O&M plan to provide specifics on the post-treatment O&M groundwater monitoring program, well/injector maintenance, any future oxidant applications; and
  - Include a reporting plan.
- Annual certification that is intended to validate that the institutional controls (and also engineering controls if required in the future) that are implemented for the Site are unchanged from the previous certification and that no circumstances have occurred that impair the ability of the controls to protect public health and the environment, or constitute a violation or failure to comply with any O&M or SMP for the Site.
- Development and implementation of an environmental easement to require compliance with the SMP and require the property owner to complete and submit to the NYSDEC the annual certification described above. In addition, the NYSDEC will be given a 60-day notice in advance of any “change of use” at the Site.

The results of the in-situ chemical oxidation work, and associated performance monitoring will be provided in an OU1 Remediation/Final Engineering Report (OU1 R/FER) for operable unit OU1. It is anticipated that at least the first two rounds of post-treatment O&M groundwater monitoring will be included in the OU1 remediation report. The SMP and environmental easement will also be included as part of the OU1 R/FER. Annual site management reports (SMRs) will be used to present subsequent post-treatment O&M groundwater monitoring events, annual certification reports, information and requirements set forth in Section 6.4(d) of DER-10 (or current version at the time the SMR is prepared) that pertain to the selected remedy and have not been presented in the OU1 R/FER or previous SMRs, and other pertinent information deemed necessary to evaluate the performance of the remedy.

Monthly progress reports for the Site will also include information pertaining to further development and implementation of the OU1 remedy as the project progresses.

This remedial work plan includes an assessment of the selected remedy, which indicated that the remedy is viable for the conditions that exist at AOC1. The assessment also identifies challenges that are faced with implementing the in-situ chemical oxidation remedy as well as some general information for solutions to those challenges. The remedial design plans will further define the challenges and solutions associated with implementing the in-situ chemical oxidation remedy using Fenton's reagent and sodium permanganate.

It is anticipated that the design and implementation of the in-situ chemical oxidation activities will take a total of twenty-five or more months to complete. Post-treatment O&M groundwater monitoring could be started within six months after completing the in-situ chemical oxidation activities, and would continue for up to five years. The institutional controls would be completed within approximately two months after completing the in-situ chemical oxidation activities. A FER could be developed within six months after completing the in-situ chemical oxidation activities.

The site-specific HASP dated November 2001, which was included as part of the General Investigation Work Plan dated June 2002 will generally be implemented during performance of the tasks presented in this OU1 Remedial Work Plan. The HASP includes a CAMP. In addition, DAY or the remediation contractor would provide a separate HASP to be implemented during activities that are associated with the in-situ chemical oxidation treatments and performance monitoring events.

The applicable quality assurance/quality control (QA/QC) protocols and procedures included in Section 5.0 of the General Investigation Work Plan dated June 2002 would be implemented during performance of the tasks presented in this OU1 Remedial Work Plan.

1.0 INTRODUCTION

This Remedial Work Plan was prepared for the subject property (Site), which consists of an approximate 33.6-acre property (addressed as 4777 Dewey Avenue) located on the west side of Dewey Avenue in the Town of Greece, County of Monroe, New York and is commonly referred to as the former Air Force Plant No. 51 (AFP51). Figures AOC1-A and AOC1-B depict the location of the Site.

This Remedial Work Plan for Operable Unit OU1 (OU1 Remedial Work Plan) was developed in accordance with the requirements of Voluntary Agreement Index #B8-590-01-02 between the NYSDEC and 4800 Dewey. The NYSDEC document titled "Draft DER-10 Technical Guidance for Site Investigation and Remediation" (NYSDEC DER-10) dated December 2002 was used in the development of this OU1 Remedial Work Plan. The OU1 Remedial Work Plan includes an evaluation of the proposed remedy in relation to factors set forth in 6 New York Codes, Rules and Regulations (NYCRR) 375-1.8 (effective December 14, 2006).

Operable Unit OU1 is comprised of the following two areas of concern (AOCs):

> **AOC1 (Former Plating Pond/Lagoon):** Information indicates that plating rinse wastewater was disposed of into a man-made plating pond/lagoon, which ultimately flowed to Round Pond Creek. Chlorinated VOCs, petroleum-related VOCs, SVOCs, and some metals have been detected in sediment, soil and/or groundwater at, or in proximity to, the former plating pond/lagoon. As an initial remedial action, surface water in the plating pond/lagoon was removed via pumping, and underlying sediments/soils were excavated down to the top of the groundwater table in 2000/2001 by the USACE. However, contamination, including DNAPL that predominantly consists of chlorinated VOCs, is still present at AOC1. As presented in the document titled "Environmental Site Investigation Report; Former Air Force Plant 51; 4777 Dewey Avenue, Greece, New York; DERP-FUDFS Site No. C02NY057500; NYSDEC Site No. V00421; Operable Unit OU1; AOC1 (Former Plating Pond/Lagoon); AOC2 (Lagoon and Stormwater Outfalls)" dated April 3, 2006, environmental work was conducted after the initial remedial action in order to further delineate the nature and extent of contamination at Operable Unit OU1. As part of this work, an IRM was commenced in July 2003 to monitor and recover DNAPL from the former plating pond/lagoon area. Over 180 gallons of DNAPL has been recovered between July 2003 and August 2006. Data limitations have not been identified for AOC1, except for the area in proximity to well MW1-7. As such, this OU1 Remedial Work Plan includes further evaluation of subsurface conditions in the area between well MW1-7 and the former plating pond/lagoon as a remedial design investigation. The results of this remedial design investigation will be used to modify details concerning the selected remedy as deemed necessary. Other areas of contamination that have been identified during investigation of AOC1 (e.g., VOCs in proximity to wells MW1-3, MW1-19 and MW1-21, and contaminants in sediment in a trench drain located inside the northwest portion of Building #1), will be further addressed under other operable units.
>
> **AOC2 (Lagoon and Stormwater Outfalls):** A discharge point associated with the former plating pond/lagoon is located west of Building #1 just outside the fence of the Site (i.e., approximate property line). The outfall area discharges onto vacant wetland-type land. The USACE remediated soil and sediments in the discharge ditch downstream of the former plating pond/lagoon, but stopped at the property line. Discharges to the former plating pond/lagoon outfall have been eliminated as a result of the USACE's remediation efforts.

> Since there are no more discharges to the former plating pond/lagoon, and since discharges from the stormwater system are being controlled, further work at AOC2 has not been requested by regulatory agencies. However, impacts to the wetlands will be addressed at a later time under Operable Unit OU7, area of concern AOC3 (off-site aquatic life). In addition, the source of contaminants present within the stormwater system is being addressed under Operable Unit OU2, area of concern AOC4 (stormwater system).

This OU1 Remedial Work Plan outlines the scope of work developed to address only contamination that is present at AOC1 (former plating pond/lagoon).

1.1 Site Background

The facilities on the Site were generally constructed in the early 1940's. The Department of Defense either owned or leased facilities situated on approximately 44 acres of land located in the Town of Greece, New York, including the Site. These facilities were used for the manufacture of ocean-going ships and cranes during and immediately following World War II, and subsequently for the manufacture of B-52 aircraft parts and Talos ground handling equipment. Information has not been obtained to suggest radioactive materials were used, stored or disposed of at the Site.

The site was declared excess to the needs of the United States Air Force, and care and custody for the site was transferred to the General Services Administration (GSA). GSA conveyed 40.33 acres fee and 3.66 acres easement to the Monroe County Water Authority (MCWA), which later conveyed 36.63 acres fee and 3.24 acres easement to Dewey Avenue, Inc. 4800 Dewey currently owns the Site.

The Site is currently bounded to the north by the Monroe County Shoremont Water Treatment Plant; to the east by Dewey Avenue, with a residential apartment complex beyond; to the west by vacant undeveloped land and New York State/Federal wetlands (containing Round Pond Creek); and to the south by the Ontario State Parkway with residential property beyond. The Site is zoned as "IL" (light industrial).

1.2 Summary of Current Subsurface Conditions

Test borings were advanced and monitoring wells were installed to evaluate the nature and extent of contaminants at AOC1, and also to monitor and recover DNAPL from AOC1 (refer to Figure AOC1-C).

Fill consisting of reworked soil (e.g., silt, clay, sand and gravel) that occasionally contained trace amounts of concrete, wood or brick is present at portions of AOC1. This fill extended from the ground surface to depths ranging between approximately 4.0 feet and 15.5 feet.

The fill material that was used to backfill the former plating pond/lagoon subsequent to completion of 2000/2001 remedial work conducted by the USACE consisted of silt and/or clay that is intermixed with lesser amounts of sand and gravel from the ground surface to depths ranging between 8 feet and 11.5 feet. This fill is then underlain by a fill material consisting of sand and/or fine gravel that has a thickness ranging between 0.5 foot and two feet. Figures AOC1-D for cross section A-A’ and Figure AOC1-E for cross section B-B’ show this fill in relation to the former plating pond/lagoon as defined in the April 3, 2006 Environmental Site Investigation Report.

At most test locations, the uppermost layer of indigenous soil consists predominantly of silt and/or clay with lesser amounts of sand and gravel. The upper bedrock encountered beneath the overburden deposits in this area of the Site consists of brick red sandstone from the Queenston Formation, Late Ordovician Period, Paleozoic Era (refer to Figures AOC1-D and AOC1-E).

As documented in the April 3, 2006 Environmental Site Investigation Report, the shallow overburden groundwater table in the area of the former plating pond/lagoon generally flows radially outward at relatively low hydraulic gradients. For January 20, 2003, January 28, 2003, April 21, 2003 and April 12, 2004, groundwater in the shallow overburden generally flowed radially outward (i.e., flows west, and east) from the former plating pond/lagoon area and in the vicinity of well MW1-5 north of the former plating pond/lagoon. On August 30, 2004, groundwater in the shallow overburden generally flowed north and west; however, groundwater in proximity to well MW1-5 flowed to the south toward the former plating pond/lagoon (refer to Figure AOC1-F). Groundwater in the deeper overburden/bedrock interface generally flows north and west.

As documented in the April 3, 2006 Environmental Site Investigation Report, the nature and extent of contamination at AOC1 are summarized as follows:

- Contamination detected in subsurface soil or groundwater at AOC1 that appears attributable to historic operations at the Site primarily consists of VOCs, SVOCs and some metals. Total VOC concentrations detected in subsurface soil samples from AOC1 are shown on Figure AOC1-G. The majority of the specific VOCs and SVOCs that were detected at concentrations exceeding standards, criteria and guidance (SCG) values are typically associated with chlorinated solvents or petroleum products.
- Some subsurface soil samples from well locations MW1-7, MW1-8, MW1-9, MW1-10, MW1-12 and MW1-13 (shown on Figures AOC1-C and AOC1-G) contained concentrations of VOCs that exceeded SCG values. Test location MW1-7 is located approximately 140 feet west of the former plating pond/lagoon along the perimeter of the Site, and the other five test locations with exceedances are located within the footprint of the former plating pond/lagoon. Due to the absence of data from the area between well MW1-7 and the former plating pond/lagoon, it is possible that subsurface soil in the area between the former plating pond/lagoon and well MW1-7 may contain VOCs at concentrations exceeding SCGs. Alternatively, it is possible that a separate VOC source exists in proximity to well MW1-7.

  VOCs were detected at concentrations exceeding SCG values in groundwater samples from 13 of 17 well locations that were tested (i.e., wells MW1-1, MW1-3 through MW1-10, and MW1-18 through MW1-21 as shown of Figure AOC1-C). Figure AOC1-H shows the total VOC concentrations detected in groundwater samples collected on the dates shown. Figure AOC1-I contours the total VOCs using the highest concentrations of VOCs detected in groundwater samples at any given well during monitoring events between January 2003 and September 2004. As shown from these figures, the highest concentrations of VOCs detected in groundwater were in samples from wells located:

  - Within the footprint of the former plating pond/lagoon (wells MW1-8, MW1-9, MW1-10);
  - Within the filled-in portion of the former channel north of building #1 (i.e., well MW1-21); and
  - In proximity to the northeast corner of Building #1 and a stormwater catch basin (i.e., wells MW1-3 and MW1-19).

[Note: The groundwater quality in proximity to well locations MW1-3, MW1-19 and MW1-21 is not addressed under this OU1 Remedial Work Plan, but will be addressed at a later time under other operable units.]

- DNAPL generally consisting of chlorinated VOCs with lesser concentrations of other VOCs, SVOCs, metals, and polychlorinated biphenyls (PCBs) was encountered at four wells (i.e., MW1-10, MW1-12, MW1-13, and MW1-14 as shown on Figure AOC1-C) within the footprint of the former plating pond/lagoon. In accordance with provisions set forth in the NYSDEC-approved Supplemental Investigation Work Plan OU1-2 dated May 2003, DNAPL has been recovered from the footprint of the former plating pond/lagoon since July 2003, and it is anticipated that this recovery work will continue until this OU1 Remedial Work Plan is implemented. Light non-aqueous phase liquid (LNAPL) has not been encountered at operable unit OU1.
- Potential sources for contamination include the following:
  - Past discharges of degreasers, plating chemicals, etc. to the former plating pond/lagoon from Site operations; and
  - Other potential unknown sources in proximity to well MW1-7.
- The majority of contamination detected is located at, or within, the saturated zone. This may be due in part to the fact that surface water, sediments, and soil were removed down to the top of the apparent groundwater table from the former plating pond/lagoon as part of remedial work conducted by the USACE in 2000/2001. Also, concentrations of contaminants tend to decrease as the distance away from the apparent source areas is increased. The vertical extent of impacted soil within the former plating pond/lagoon was not fully defined; however, analytical laboratory test results for soil samples obtained from deeper overburden/bedrock wells set immediately outside the footprint of the former plating pond/lagoon (i.e., wells MW1-16, MW1-17 and MW1-18) showed VOC concentrations do not exceed recommended soil cleanup objectives (RSCOs) as referenced in the NYSDEC document titled "*Division of Technical and Administrative Guidance Memorandum: Determination of Soil Cleanup Objectives and Cleanup Levels*" (TAGM 4046) dated January 24, 1994, as amended by the NYSDEC's supplemental Tables dated August 22, 2001).
- Analytical laboratory test results for groundwater samples indicate that some VOCs are present in groundwater at concentrations above SCGs in perimeter wells located west, north and east of the former plating pond/lagoon. However, the concentrations of VOCs detected at these perimeter wells are significantly lower than the concentrations of VOCs detected within, or in proximity to, the former plating pond/lagoon.
- Based on the studies performed, the majority of contaminated soils and groundwater exceeding SCGs for VOCs and/or SVOCs at AOC1 generally remain on-site within, and in proximity to, the former plating pond/lagoon.
- Metals were detected in subsurface soil and groundwater samples collected from OU1 locations on the Site. However, the presence of many of these metals may be attributable to naturally occurring conditions. In some instances, occasional elevated concentrations of specific metals (e.g., iron, mercury, zinc, etc.) that were detected in soil or groundwater may be indicative of localized impacts attributable to historic operations at the Site. However, a correlation of metals exceeding SCGs in soil, groundwater and/or DNAPL was not apparent.

In general, it appears that the majority of contamination (e.g., VOCs, SVOCs, metals, PCBs, etc.) discharged to the former plating pond/lagoon was remediated as a result of the 2000/2001 remedial work conducted by the USACE. However, residual contamination primarily consisting of chlorinated VOCs with lesser amounts of other constituents generally remains in subsurface soil below the water table and in the groundwater.

1.3 Project Objectives and Remedial Action Objectives

The primary objective of the proposed scope of work outlined in this OUI Remedial Work Plan is to eliminate or mitigate contamination that exists at area of concern AOC1 (former plating pond/lagoon). As another objective, subsurface conditions would be monitored to evaluate the effectiveness of the remedy. Remedial action objectives (RAOs) for contamination detected in soil and groundwater are provided as follows:

<u>Soil</u>

RAOs for public health protection include:

- Prevent ingestion and direct contact with contaminated soil.
- Prevent inhalation of, and exposure to, volatilization of contaminants in soil.

RAOs for environmental protection include:

- Prevent migration of contamination in soil that would result in impacts to surface water or groundwater.
- Prevent impacts to biota via ingestion or direct contact with contaminated soil that would result in toxic conditions or impacts from bioaccumulation through the terrestrial food chain.

<u>Groundwater</u>

RAOs for public health protection include:

- Prevent ingestion of groundwater with contaminant levels exceeding drinking water standards.
- Prevent contact with, or inhalation of, volatiles from contaminated groundwater.

RAOs for environmental protection include:

- Remove the source of groundwater contamination. This involves removal/treatment of DNAPL and other grossly contaminated media to the extent deemed feasible while achieving the lower of the Protection of Public Health (Commercial) soil cleanup objectives (SCOs) or Protection of Groundwater SCOs (to the extent deemed feasible) as referenced in Section 375-6 of the NYSDEC document titled “*6 NYCRR Part 375, Environmental Remediation Programs*” dated December 14, 2006.
- Restore the groundwater aquifer to pre-disposal/pre-release conditions by achieving groundwater standards and guidance values (to the extent deemed feasible) that are referenced in the NYSDEC Division of Water Technical and Operational Guidance Series 1.1.1 document titled "*Ambient Water Quality Standards and Guidance Values and Groundwater Effluent Limitations*" (TOGS 1.1.1) dated June 1998 (as amended by an April 2000 addendum).

- Prevent off-site migration of OU1 contaminants exceeding TOGS 1.1.1 groundwater standards and guidance values
- Prevent the discharge of contaminants to surface water.

2.0 REMEDIAL DESIGN INVESTIGATION

A remedial design investigation would initially be performed to further evaluate/define the extent of VOC impact to soil and groundwater on the Site in the area generally between existing monitoring well MW1-7 and the former plating pond/lagoon. Additional goals of the remedial design investigation include:

- Obtaining information that can be used for the selection and design of the remedial program for the area between MW1-7 and the former plating pond/lagoon. It is assumed that one or more of the remedial elements identified in Section 3 of this work plan will be selected to this area between MW1-7 and the former plating pond/lagoon. A Remedial Work Plan modification will be made if this assumption is incorrect.

- Obtaining information that can be used to fill data gaps, if any, in order to complete the overall remedial design for OU1. If data gaps remain, supplemental Remedial Design Investigation Work Plan(s) will be developed and submitted for NYSDEC approval.

The proposed remedial design investigation consists of the tasks listed below.

Soil Evaluation

Nine test borings will be advanced in the general area between well MW1-7 and the former plating pond/lagoon. It is anticipated that test borings will be advanced to depths up to twenty feet below the ground surface using direct-push drilling and sampling equipment. To the extent practicable, continuous soil samples will be collected from the existing ground surface to the final depth of each test boring. The anticipated locations of these test borings are shown on Figure AOC1-J; however, the actual locations may vary depending upon site conditions encountered and field decisions made with concurrence from the on-site NYSDEC Site representative.

The work completed will be monitored and documented. Monitoring will include visual observations of soil samples (e.g., staining, odors, etc.) as well as screening the headspace on portions of samples with a photoionization detector (PID) for evidence of VOC impact. Other portions of the samples will be collected for possible laboratory analysis.

Up to one soil sample from each test boring (i.e., a total of up to nine soil samples) will be selected and subsequently tested by a New York State Department of Health (NYSDOH) Environmental Laboratory Approval Program (ELAP) certified analytical laboratory for target compound list (TCL) VOCs using Analytical Services Protocol (ASP) Method OLM04.2 and target analyte list (TAL) metals using ASP Method ILM04.1. The analytical laboratory test results will be compared to appropriate SCGs that are available at the time of reporting, such as: Soil cleanup objectives (SCOs) for Protection of Public Health (Commercial) SCOs and Protection of Groundwater as referenced in the NYSDEC document titled "*6 NYCRR Part 375 Environmental Remediation Program*"; dated December 14, 2006.

As part of the quality assurance/quality control for this project, one field blank from soil sampling equipment will be analyzed for TCL VOCs using ASP Method OLM04.2 and TAL Metals using ASP Method ILM04.1, and a matrix spike/matrix spike duplicate (MS/MSD) will also be performed on one of the soil samples.

Groundwater Evaluation

One of the test borings will be converted into a one-inch polyvinyl chloride (PVC) groundwater monitoring well. The anticipated location of the test boring that will be converted to a groundwater monitoring well is shown on the Figure AOC1-J; however, the actual location may vary depending upon actual site conditions encountered and field decisions made with concurrence from the on-site NYSDEC Site representative. The groundwater monitoring well will be constructed of one-inch inner diameter PVC with a ten-foot long 10-slot screen attached to solid riser. It is anticipated that the well screen will be placed from about 5.5 feet and 15.5 feet below the existing ground surface (i.e., similar screened depth interval of existing wells MW1-7, MW1-8 and MW1-11). The annulus around and at least one foot above the screen will be backfilled with a sand pack. A minimum two-foot thick bentonite seal will be placed above the sand pack and the remaining annulus will be filled with cement/bentonite grout. A steel protective casing or curb box will be placed over the monitoring well and sealed in place with concrete.

Approximately one week following installation, the new well will be developed by utilizing either a new dedicated bailer with dedicated cord, or a centrifugal pump and dedicated tubing. No fluids will be added to the well during development. The well development procedure will be as follows:

- Obtain a pre-development static water level reading;
- Calculate water/sediment volume in the well;
- Obtain initial field water quality measurements (e.g., pH, conductance, turbidity, temperature, and PID readings);
- Monitor for the presence of LNAPL or DNAPL;
- Select development method and set up equipment depending on method used;
- Alternate water agitation methods (e.g., moving a bailer or pump tubing up and down inside the screened interval) and water removal methods (e.g., pumping or bailing) in order to suspend and remove solids from the well;
- Obtain field water quality measurements for every one to five gallons of water removed. Record water quantities and rates removed;
- Stop development when water quality criteria are met and at least five well volumes have been removed;
- Obtain post-development water level readings; and
- Document development procedures, measurements, quantities, etc.

Development will continue until the following criteria is achieved:

- Water is clear and free of sediment and turbidity is less than 50 nephelometric turbidity units (NTUs);
- Monitoring parameters have stabilized (i.e., pH is ±0.1 unit; conductance is ±3%, temperature and other parameters are ±10%); and
- A minimum of five well volumes has been removed.

The field measurement data will be presented on Monitoring Well Development Logs.

One groundwater sample will be collected from the new well and also existing wells MW1-6, MW1-7, MW1-8 and MW1-11 (i.e., a total of five well locations). The samples will be collected using low-flow purge and sample techniques with a bladder pump connected to a control box. The low-flow sampling method is ideal for collecting in-line groundwater samples and dissolved oxygen readings. The low-flow purging and sampling procedures to be utilized are outlined below:

- Prior to purging and sampling, static water level measurements will be taken from each well using an oil/water interface meter. The results of this work will be documented in the field.

- In order to minimize the potential re-suspension of solids in the bottom of the well, well depths will not be measured prior to or during low-flow purging and sampling. Well depth information will be obtained from: 1) measurements collected during well development; 2) from well logs; or 3) will be measured after sampling is completed.

- A portable bladder pump connected to new disposable polyethylene tubing will be lowered and positioned at or slightly above the mid-point of the well screen when the screened interval is set in relatively homogeneous material. When the screened interval is set in heterogeneous materials, the pump will be positioned adjacent to the zone of highest hydraulic conductivity (as defined by geologic samples). Care will be taken to install and lower the bladder pump slowly in order to minimize disturbance of the water column.

- The pump will be connected to a control box that is operated on compressed gas (nitrogen, air, etc.) and is capable of varying pumping rates. An in-line flow-through cell attached to a Horiba U-22 water quality meter (or similar equipment) will be connected to the bladder pump effluent tubing to measure water quality data.

- The pump will be started at a pumping rate of 100 ml/min or less (for pumps that can not achieve a flow rate this low, the pump will be started at the lowest pump rate possible). The water level in the well will be measured and the pump rate will be adjusted (i.e., increased or decreased) until the drawdown is stabilized. In order to establish the optimum flow-rate for purging and sampling, the water level in the well will be measured on a periodic basis (i.e., every one or two minutes) using an electronic water level meter or an oil/water interface meter. When the water level in the well has stabilized (i.e., use goal of <0.33 ft of constant drawdown), the water level measurements will be collected less frequently.

- While purging the well at the stabilized water level, water quality indicator parameters will be monitored on a three to five minute basis with a Horiba U-22 water quality meter (or similar equipment). Water quality indicator parameters will be considered stabilized after three consecutive readings for each of the following parameters are generally achieved:

  - pH (± 0.1);
  - specific conductance (± 3%);
  - dissolved oxygen (± 10 %);
  - oxidation-reduction potential (± 10 mV);
  - temperature (± 10%); and
  - turbidity (± 10%, when turbidity is greater than 10 NTUs)

- Following stabilization of the water quality parameters, the flow-through cell will be disconnected and a groundwater sample will be collected from the bladder pump effluent tubing. The pumping rate during sampling will remain at the established purging rate or it may be adjusted downward to minimize aeration, bubble formation, or turbulent filling of sample containers. A pumping rate below 100 ml/min will be used when collecting VOC samples.

- The procedures and equipment used during the purging and groundwater sampling and the field measurement data will be documented in the field and recorded on Monitoring Well Sampling Logs.

- For wells set in low-permeability formations and fractured bedrock (if encountered), alternative purging and sampling techniques from those specified above may become necessary. Any changes in technique shall be presented and approved by the on-site NYSDEC site representative.

The groundwater samples will be submitted to a NYSDOH ELAP-certified analytical laboratory, which will analyze the samples for TCL VOCs using NYSDEC ASP Method OLM04.2, and TAL metals using ASP Method ILM04.1. Natural attenuation and water quality parameters such as dissolved oxygen, oxidation-reduction potential, pH, temperature, conductivity, turbidity, nitrate, iron (II), manganese, sulfate, methane, and chloride will also be obtained using a Horiba U-22 water quality meter (or similar equipment) and analytical laboratory testing (i.e., Methods SM3500D, E300IC, SW6010B, and RSK175). The TCL VOCs and TAL metals test results will be compared to groundwater standards and guidance values as referenced in NYSDEC TOGS 1.1.1.

As part of the quality assurance/quality control for this project, one field blank from groundwater sampling equipment will be analyzed for TCL VOCs using ASP Method OLM04.2 and TAL Metals using ASP Method ILM04.1, one trip blank will be analyzed for TCL VOCs using ASP Method OLM04.2, and an MS/MSD will also be performed on one of the groundwater samples.

The locations of the test borings and new well will be surveyed, and the horizontal coordinates (northings and eastings) will be provided in meters using the NAD83UTM Zone 18 (NYTM) coordinate system. The elevation of the new well will be surveyed in feet using the same vertical datum that was used for existing wells. Static water levels will be obtained from each OU1 overburden groundwater monitoring well, including the new well. Groundwater elevations will be calculated, and a potentiometric groundwater contour map for the uppermost water-bearing unit intercepted by these overburden wells will be developed.

The work performed as part of the remedial design investigation will be documented in a data package, which includes: applicable figures; boring logs; a well construction diagram; well sampling logs; analytical laboratory reports and chain-of-custody documentation; and data tables comparing the test results to regulatory SCGs. To the extent deemed necessary, the results of the remedial design investigation will be used to design the remedial actions specified herein with concurrence from the NYSDEC.

3.0 REMEDIAL ACTIVITIES

The proposed remedy selected to address contamination at operable unit OU1 area of concern AOC1 (former plating pond/lagoon) consists of the following components:

- In-Situ Chemical Oxidation of the On-Site Source Area
- Post-Treatment O&M Groundwater Monitoring
- Institutional Controls

A NYSDEC "Transform the Past….Build for the Future" sign will be posted while remedial activities are being performed at the Site. The components of the proposed remedy are further discussed below.

3.1 In-Situ Chemical Oxidation of the On-Site Source Area

In-situ chemical oxidation will be conducted in subsurface soils and groundwater in the source area (i.e., generally an approximate 100-foot by 140-foot area within, and around, the former plating pond/lagoon location). This in-situ remediation is intended to destroy contaminants of concern (e.g., VOCs) within the source area at area of concern AOC1. Geo-Cleanse International, Inc. (GCI), or a comparable remediation contractor, will be retained to perform remediation services using hydrogen peroxide with a site-specific formulated catalyst (Fenton's reagent) and sodium permanganate. A copy of GCI's Statement of Qualifications (SOQ) is attached in Appendix B. The SOQ includes technical information (injector construction, chemicals, etc.), performance information on other projects, and safety provisions. Permits required to complete the remedy will be obtained as deemed necessary.

In-situ chemical oxidation is the process of oxidizing contaminants in the groundwater and soil by injecting water containing high concentrations of an oxidant to the area of contamination. This technology can eliminate many organic contaminants in both saturated and unsaturated environments by changing the organic contaminants into harmless materials, such as water and carbon dioxide. A copy of a United States Environmental Protection Agency (USEPA) document titled "In-Situ Chemical Oxidation" dated 2006 by S.G. Huling and B.E Pivetz is included in Appendix C, and this document provides information regarding in-situ chemical oxidation. Some general aspects of chemical oxidation using Fenton's reagent and sodium permanganate are further discussed below:

<u>Fenton's Reagent</u>

The Fenton's reagent reaction ($H_2O_2 + Fe^{+2} \rightarrow OH^{\cdot} + OH^{-} + Fe^{+3}$) was reported in 1898 by H.J.H Fenton. GCI modified this chemistry for use in its in-situ environmental applications, which has resulted in an aggressive, low pressurized injection of concentrated hydrogen peroxide (H_2O_2) and ferrous iron (Fe^{+2}) catalyst that generates the hydroxyl free radical ($OH^{\cdot}$), which is the active oxidizing agent. The hydroxyl free radical is a non-selective oxidant. Oxidation of an organic compound by the hydroxyl free radical is rapid and exothermic (heat-producing) and results in the reduction of contaminants to primarily carbon dioxide and oxygen ($OH^{\cdot}$ + organic contaminant $\rightarrow CO_2 + H_2O$).

Types of organic contaminants treated using Fenton's reagent for in-situ chemical oxidation include petroleum hydrocarbons, chlorinated ethanes (e.g., 1,1,1-trichloroethane), chlorinated ethenes (e.g., tetrachloroethene, trichloroethene, dichloroethenes, vinyl chloride), manufactured gas plant wastes (e.g., polycyclic aromatic hydrocarbons), and free phase LNAPL and DNAPL.

Sodium Permanganate

Sodium permanganate ($NaMnO_4$) is a strong oxidizer, but not as strong as the hydroxyl free radical generated by Fenton's reagent. The exact chemical reaction is dependent upon the organic contaminants present and the oxidant utilized. The general reaction that occurs between permanganate and an organic contaminant is as follows: $NaMnO_4$ + Organic Contaminant → CO_2 + MnO_2 + dissolved salts (e.g., Na).

Types of organic contaminants treated using sodium permanganate for in-situ chemical oxidation include chlorinated ethenes (e.g., tetrachloroethene, trichloroethene, dichloroethenes, vinyl chloride). Sodium permanganate does not readily oxidize petroleum hydrocarbons, chlorinated ethanes (e.g., 1,1,1-trichloroethane), LNAPL, or DNAPL.

The chemical oxidation remedial work is divided into a Pilot Phase, a Full-Scale (Primary) Phase, and a Polishing Phase (if deemed necessary). Certain assumptions are made regarding reagent requirements, reagent injection rates, radius of influence of injection points and number of injection points. Some assumptions used include: hardness of groundwater is less than 200 ppm; an average of 293 ppm of chlorinated VOCs is sorbed to saturated soil in the Pilot Phase treatment area; the average concentration of dissolved chlorinated VOCs in groundwater is approximately 558 ppm in the Pilot Phase treatment areas, an average concentration of one ppm of chlorinated VOCs is sorbed to saturated soils in the Full-Scale Phase treatment area, and the average concentration of dissolved chlorinated VOCs in groundwater is 224 ppm in the Full-Scale Phase treatment area. Based on currently available Site data, the preliminary time and dosage estimates account for the presence and destruction of mobile and residual DNAPL during the Pilot Phase treatment, and assumes that DNAPL is not present during the Full-Scale (Primary) Phase treatment or the Polishing Phase treatment (if deemed necessary). The actual amount of chemical oxidants are based on the higher of stoichiometric requirements or minimum volume of oxidant needed to treat within each injector's radius of influence using the Site data and various assumptions, including those identified above.

GCI has estimated that a total of approximately 139,500 pounds of 50% hydrogen peroxide and 1,840 pounds of 40% sodium permanganate are required for the chemical oxidation. The 50% hydrogen peroxide is a powder that will be mixed with water to create an injectate with a density that is expected to be less than 1.08. The 40% sodium permanganate is a liquid that will be mixed with water to create an injectate with a density that is expected to be less than 1.02. GCI estimates that approximately 4,000 pounds of 50% hydrogen peroxide and site-specific catalyst can be injected per day with one injection vehicle. Further specifics on the remediation program are provided below.

3.1.1 Pilot Phase

A Pilot Phase Remedial Design Plan will be prepared and approved by regulatory agencies before implementing Pilot Phase field activities. This plan will include: a sampling plan; a health and safety plan; and details concerning injector construction, mixing and application of injectates, process monitoring, and performance monitoring. The Pilot Phase will first evaluate Fenton's reagent and subsequently evaluate sodium permanganate.

It is anticipated that the Pilot Phase treatment will be conducted over an approximate 50-foot by 50-foot area near former well MW1-10 (refer to Figure AOC1-K). The Pilot Phase treatment will focus on treating contamination present in an approximate ten-foot thick layer that is situated between approximately 8 and 18 feet, or 10 and 20 feet, below the ground surface.

It is currently anticipated that the objectives of the Pilot Phase will include the following:

- Evaluate travel times, distribution patterns (vertical and lateral), treatment effectiveness (vertical and lateral) and persistence of oxidants and reagents.
- Determine whether Full-Scale Phase chemical oxidation application is feasible, or if an alternative remedy should be evaluated.
- Evaluate the need for VOC and DNAPL migration control measures.
- Evaluate the potential for metals mobilization and attenuation in groundwater.
- Evaluate whether multi-level injectors are needed to treat the full vertical extent of the source area, including in the area of more permeable fill within the former plating pond/lagoon that is underlain by less permeable native soil.
- Assess contaminant rebound and determine if multiple injections of Fenton's reagent or sodium permanganate may be needed to meet the RAOs.
- Document any problems that occur in the field during implementation of the Pilot Phase, and develop associated corrective measures to be used during the Full-Scale Phase.
- Develop injection procedures that are optimized for the Site, such as injection rates pressures, depths, etc.
- Develop monitoring procedures for evaluating performance during the Pilot Phase treatment, and identify appropriate monitoring procedures for the Full-Scale Phase treatment.
- Obtain other data (if necessary) that can be used to design the Full-Scale Phase treatment.

GCI has estimated that nine vertical injectors will be installed within the Pilot Phase treatment area. A subcontractor will be retained to provide direct-push Geoprobe equipment to advance the borings at injector locations. Continuous soil samples will be collected from approximately 30% of the locations during injector installation in order to adjust actual depths and locations where reagents are to be injected. One of these injector locations will be advanced to a depth that will assist in defining the vertical extent of contamination within the former plating pond/lagoon. It is anticipated that the injectors will be screened within depth intervals with the highest field evidence of VOCs (i.e., elevated PID readings, staining, odors, etc) on soil samples that are collected from injectors.

One soil sample and one groundwater sample from three injector locations, and groundwater samples from up to six existing wells within or in proximity to the footprint of the former plating pond/lagoon, will be analyzed by a NYSDOH ELAP-certified analytical laboratory for TCL VOCs using NYSDEC ASP Method OLM04.2 and TAL Metals using ASP Method ILM04.1.

The NYSDEC will be consulted regarding the injector locations and existing monitoring well locations that are selected for sampling. Groundwater samples will be collected using low-flow sampling techniques (described in Section 2.0 of this OU1 Remedial Work Plan) or another technique (i.e., conventional purge and sample with disposable bailer, disposable diffusion bag samplers, etc.) that is acceptable to the NYSDEC. Water quality parameters such as dissolved oxygen, oxidation-reduction potential, pH, temperature, conductivity and turbidity may also be obtained using a Horiba U-22 water quality meter (or similar equipment). The analytical laboratory test results will be compared to appropriate NYSDEC Part 375 SCOs and TOGS 1.1.1 groundwater standards and guidance values. GCI may arrange for some of the samples to be analyzed for other parameters to assist in formulating a Fenton's reagent catalyst that is tailored for the Site's groundwater chemistry.

Each injector will be constructed of 0.75-inch inner-diameter Schedule 80 chlorinated polyvinyl chloride (CPVC) that has 10-slot or 20-slot screened sections connected to a solid riser. It is anticipated that each injector will have a five-foot length of screen; however, screened intervals may be adjusted based on actual field conditions encountered. The necessary connectors will be constructed at or near the ground surface for delivery of the reagents. Further injector construction details are provided in the GCI SOQ that is attached in Appendix B.

Four vent wells will also be installed within the Pilot Phase treatment area. It is anticipated that each well will be installed to a depth that intercepts the top of the uppermost water-bearing zone. These vent wells will be installed using direct-push equipment, and construction details will be provided in the Pilot Phase Remedial Design Plan. The vent wells will be used to relieve gas building-up (if present) during chemical oxidation using Fenton's reagent and for process monitoring during the Pilot Phase injection work.

Based on current available data, GCI estimates that 27,000 pounds of 50% hydrogen peroxide will be injected along with a site-specific GCI catalyst, which will result in a 3% to 12% actual hydrogen peroxide percentage being injected. Based on currently available data, the preliminary time and dosage estimates account for the presence of some mobile and residual DNAPL during the Pilot Phase treatment. Actual amounts and concentrations of chemical oxidation materials will be refined based on the baseline testing data.

The hydrogen peroxide and catalyst will then be injected over an approximate 10-day period using one injection vehicle. During this Pilot Phase, GCI will conduct a radius of influence test to determine the quantity of oxidant required in order to establish connectivity of oxidant between injectors. This amount will be used as a baseline minimum per injector. Reagents will then be delivered at the other injectors proportionally based on contaminant concentrations throughout the Pilot Phase treatment area. Data and monitoring will be used to target areas where additional treatment is needed. As a result, it is anticipated that injectors will not receive the same amounts of reagents. In addition, it is anticipated that other components of process monitoring (e.g., equipment flow rates; effects on groundwater table; groundwater temperature, pH, etc. at nearby monitoring wells and injector points; etc.) will be completed as part of the Pilot Phase field activities. It is anticipated that the process monitoring will be performed prior to, during and immediately after application of injectates. Further details pertaining to the process monitoring will be provided in the Pilot Phase Remedial Design Plan.

Subsequent to completing performance monitoring associated with the Fenton's reagent treatment (described below), GCI will return to the Site and complete the second part of the Pilot

Phase by injecting an estimated 306 pounds of sodium permanganate at the same nine injectors previously used to inject the Fenton's reagent. Actual quantities to be injected may be modified based on the performance monitoring results obtained after the Fenton's reagent Pilot Phase application. Process monitoring and performance monitoring (described below) will also be completed as part of the Pilot Phase that involves the use of sodium permanganate.

Performance Monitoring of Pilot Phase Treatment

Subsequent to completing each part of the Pilot Phase chemical oxidation treatments, (i.e., first with Fenton's reagent, and later with sodium permanganate), performance monitoring will be performed to obtain data for use in evaluating the results of the Pilot Phase. Performance monitoring may include, but not be limited to: analysis of soil samples and groundwater samples for TCL VOCs and TAL metals; evaluation of the presence of residual injectate and related chemical reaction products; hydraulic conductivity testing; evaluation of groundwater flow; and collection of water quality parameters such as dissolved oxygen, oxidation-reduction potential, pH, temperature, conductivity, and turbidity. The analytical laboratory test results will be compared to applicable NYSDEC Part 375 SCOs and TOGS 1.1.1 groundwater standards and guidance values. Further details pertaining to the performance monitoring conducted during evaluation of the Fenton's reagent application and sodium permanganate application will be provided in the Pilot Phase Remedial Design Plan.

The findings of the Pilot Phase treatment using both the Fenton's reagent and the sodium permanganate, including their corresponding process monitoring and performance monitoring results, will be provided in a Pilot Phase report. The report will include: a summary of the work performed; figures showing well locations, injector locations, potentiometric groundwater contours, etc.; as-built drawings for the injection system(s); actual dosage rates for each location; an identification and explanation for any deviations from the Pilot Phase Remedial Design Plan; a description of any problems encountered and their resolution; a description of the effectiveness of the remedy including comparisons to RAOs; any waste stream and disposal documentation; selected photographs; boring logs; analytical laboratory data and associated chain-of-custody documentation; tables for baseline and performance monitoring data; and a discussion concerning the data as they relate to the objectives of the Pilot Phase.

3.1.2 Full-Scale Phase

A Full-Scale Phase Remedial Design Plan will be prepared and approved by regulatory agencies before implementing Full-Scale Phase field activities. The findings of the Pilot Phase will be considered when developing the Full-Scale Phase Remedial Design Plan. This plan will also include: a sampling plan; a health and safety plan; and details concerning injector construction, mixing and application of injectates, process monitoring and performance monitoring.

Based on currently available information and data, it is anticipated that Full-Scale Phase in-situ chemical oxidation treatment will be conducted over an approximate 100-foot by 140-foot area within, and in proximity to, the former plating pond/lagoon (refer to Figure AOC1-K). It is currently anticipated that the Full-Scale Phase will generally focus on treating contamination present in an approximate 10-foot thick layer that is situated between approximately 8 and 18 feet, or 10 and 20 feet, below the ground surface. However, the Full-Scale Phase will be designed to treat the full vertical extent of contamination within the defined treatment area to the degree deemed feasible. If necessary, multi-level injections will be completed over the vertical depth interval to be treated. Based on current data, GCI has estimated that 45 Full-Scale Phase vertical injectors will be installed within the Full-Scale Phase treatment area. It is anticipated that the screened intervals for the injectors will be selected based on field conditions encountered (e.g., intervals with highest field evidence of contamination) and the results of the Pilot Phase treatment. It is anticipated that the injectors installed during the Full-Scale Phase will be constructed of the same materials as described for the Pilot Phase.

A subcontractor will be retained to provide direct-push Geoprobe equipment to advance the borings at injector locations. Continuous soil samples will be collected from approximately 30% of the locations during injector installation in order to adjust actual depths and locations where reagents are to be injected. Two of these injector locations will be advanced to depths that will assist in defining the vertical extent of contamination within the former plating pond/lagoon.

One soil sample and one groundwater sample from fourteen injector locations, and up to six groundwater samples from existing monitoring wells within or in proximity to the footprint of the former plating pond/lagoon, will be analyzed by a NYSDOH ELAP-certified analytical laboratory for TCL VOCs and TAL Metals using NYSDEC ASP Method OLM04.2 to assist in estimating the baseline mass to be treated. The NYSDEC will be consulted regarding the injector locations that are selected for sampling. Groundwater samples will be collected using low-flow sampling techniques (described in Section 2.0 of this OU1 Remedial Work Plan) or another technique that is acceptable to the NYSDEC. Water quality parameters such as dissolved oxygen, oxidation-reduction potential, pH, temperature, conductivity, and turbidity may also be obtained using a Horiba U-22 water quality meter (or similar equipment). The analytical laboratory test results will be compared to appropriate NYSDEC Part 375 SCOs and TOGS 1.1.1 groundwater standards and guidance values.

Twelve additional vent wells will be installed within the Full-Scale Phase treatment area. It is anticipated that each well will be installed to a depth that intercepts the top of the uppermost water-bearing zone; however, information obtained during the Pilot Phase will be used to refine actual depths. These vent wells will be installed using direct-push equipment, and construction details will be provided in the Pilot Phase Remedial Design Plan. These twelve vent wells, and the four vent wells installed as part of the Pilot Phase, will be used to relieve gas building-up (if present) during chemical oxidation using Fenton's reagent and for process monitoring during the Full-Scale Phase injection work.

Based on current available data, GCI estimates that it will inject 112,500 pounds of 50% hydrogen peroxide along with a site-specific GCI catalyst, which will result in a 3% to 12% actual hydrogen peroxide percentage being injected. Based on currently available data, the preliminary time and dosage estimates assume that DNAPL is treated during the Pilot Phase, and that mobile and residual DNAPL are generally not present during the Full-Scale Phase. Actual amounts and concentrations of chemical oxidation materials will be refined based on the Pilot Phase data, and soil and groundwater data. Reagents will then be delivered at the injectors proportionally based on contaminant concentrations throughout the Full-Scale Phase treatment area. Currently, GCI estimates it will take 29 days to inject the hydrogen peroxide and catalyst using one injection vehicle. Components of the process monitoring used for the Pilot Phase will also be conducted during the Full-Scale Phase.

Performance Monitoring of Full-Scale Phase Treatment

Subsequent to completing the Full-Scale Phase chemical oxidation treatment work, performance monitoring will be performed to obtain data for use in evaluating the results of the Full-Scale

Phase. Performance monitoring may include, but not be limited to: analysis of soil samples and groundwater samples for TCL VOCs and TAL metals; evaluation of the presence of residual injectate and related chemical reaction products; hydraulic conductivity testing; evaluation of groundwater flow; and collection of water quality parameters such as dissolved oxygen, oxidation-reduction potential, pH, temperature, conductivity, and turbidity. The analytical laboratory test results will be compared to applicable NYSDEC Part 375 SCOs and TOGS 1.1.1 groundwater standards and guidance values.

The findings of the Full-Scale Phase process monitoring and performance monitoring will be used to assist in evaluating the effectiveness of the treatment and determining if the Polishing Phase treatment is warranted at that time.

3.1.3 Polishing Phase

If deemed necessary based on the post Full-Scale Phase treatment performance monitoring results, or based on the post-treatment O&M groundwater monitoring (refer to Section 3.2), GCI will complete a Polishing Phase treatment using sodium permanganate at existing injector locations (i.e., up to nine of the injectors installed during the Pilot Phase treatment, and up to 45 of the injectors installed during the Full-Scale Phase treatment).

A Polishing Phase Remedial Design Plan will be prepared and approved by regulatory agencies before implementing Polishing Phase field activities. The findings of the Pilot Phase and Full-Scale Phase will be considered when developing this Polishing Phase Remedial Design Plan. This plan will also include: a sampling plan; a health and safety plan; and details concerning injector construction, mixing and application of injectates, process monitoring and performance monitoring.

For the purposes of this OU1 Remedial Work Plan, GCI has estimated that approximately 1,532 pounds of 40% sodium permanganate will be injected over a 5-day period by one injection vehicle. The preliminary time and dosage estimates assume mobile and residual DNAPL are not present within the Polishing Phase treatment area based on currently available data. Actual amounts and concentrations of chemical oxidation materials will be refined based on the post Full-Scale Phase treatment performance monitoring data. Reagents will then be delivered at the injectors proportionally based on contaminant concentrations within the Full-Scale Phase treatment area.

<u>Performance Monitoring of Polishing Phase Treatment</u>

Subsequent to completing the Polishing Phase chemical oxidation treatment work, performance monitoring will be performed to obtain data for use in evaluating the results of the Polishing Phase. Performance monitoring may include, but not be limited to: analysis of soil samples and groundwater samples for TCL VOCs and TAL metals; evaluation of the presence of residual injectate and related chemical reaction products; hydraulic conductivity testing; evaluation of groundwater flow; and collection of water quality parameters such as dissolved oxygen, oxidation-reduction potential, pH, temperature, conductivity, and turbidity. The analytical laboratory test results will be compared to applicable NYSDEC Part 375 SCOs and TOGS 1.1.1 groundwater standards and guidance values. The analytical laboratory test results will be compared to applicable NYSDEC Part 375 SCOs and TOGS 1.1.1 groundwater standards and guidance values.

The findings of the Polishing Phase process monitoring and performance monitoring will be used to assist in evaluating the effectiveness of the treatment and determining if further treatments or implementation of a contingency remedy are warranted.

3.2 Post-Treatment O&M Groundwater Monitoring

Subsequent to completion of the in-situ chemical oxidation, a post-treatment operation and maintenance (O&M) groundwater monitoring program will be implemented using the AOC1 groundwater monitoring wells that exist at that time in order to evaluate the effectiveness of natural attenuation, the presence and concentration of VOCs, and to determine the extent and potential movement of contamination. This groundwater monitoring will continue for a period of up to five years. It is assumed that the wells will be sampled on a quarterly basis during the 1st year, and on a bi-annual basis for the 2nd through 5th years. As part of this monitoring program, groundwater will be tested for parameters that evaluate the effectiveness of the remedy, and evaluate natural attenuation and potential movement of any residual constituents.

It is anticipated that during each round of groundwater sampling, samples from up to eight groundwater monitoring wells will be collected using the low-flow sampling protocol described in Section 2.0, or by another technique that is acceptable to the NYSDEC. The specific wells to be sampled, a detailed sampling schedule, and other details for the post-treatment O&M groundwater monitoring will be included in the SMP. The NYSDEC will be consulted regarding the wells that are selected for sampling. A NYSDOH ELAP-certified analytical laboratory will be retained to analyze the groundwater samples collected during each sampling event for TCL VOCs using NYSDEC ASP Method OLM04.2. Water quality parameters such as dissolved oxygen, oxidation-reduction potential, pH, temperature, conductivity, and turbidity may also be obtained using a Horiba U-22 water quality meter (or similar equipment).

With approval from regulatory agencies, the duration and frequency of the groundwater monitoring, the list of parameters to be tested, and the sampling techniques (e.g., switch to use of passive diffusion samplers since only VOCs to be monitored, etc.) may be modified based on observations and the test results of samples collected during previous monitoring events.

Potential outcomes of the post-treatment O&M groundwater monitoring include closure of the operable unit, further monitoring of the operable unit, additional chemical oxidant injections at the operable unit, or selection and implementation of a contingency remedy. The additional chemical oxidant injections or contingency remedy would be intended to address any residual contamination, including DNAPL, that acts as a source of groundwater contamination resulting in off-site migration above SCGs to the extent feasible. A Supplemental Work Plan would be developed and submitted to the regulatory agencies for approval prior to implementation.

3.3 Remediation-Derived Wastes

Remediation-derived wastes (e.g., water removed from wells, decontamination water, general refuse, etc.) will be characterized, transported, and disposed off-site in accordance with applicable regulations.

3.4 Institutional Controls

It is proposed that institutional controls be implemented that include the following elements:

- Development and implementation of a Site Management Plan (SMP) to address the characterization, handling, and disposal/re-use of any media (e.g., soil, fill, groundwater) that is disturbed during any future activities at the Site. Some components of the SMP will apply to the entire Site while other components will be specific to individual operable units. As such, the SMP will be updated as each operable unit is addressed and Site conditions change. The SMP will also evaluate the potential for vapor intrusion into any future buildings to be constructed on the Site in the areas of AOC1, including requirements to mitigate such potential vapor intrusions through use of environmental engineering controls (e.g., sub-slab vapor barrier, sub-slab ventilation system, etc.) or other means. In addition, the SMP will identify use restrictions for the Site (e.g., property development and groundwater use restrictions, etc.). The SMP would also include a HASP and a CAMP to assist in reducing potential exposures to Site contaminants. Other components of the SMP would be an O&M plan to provide specifics on the post-treatment O&M groundwater monitoring program, well/injector maintenance, any future oxidant applications, and a reporting plan.
- Annual certification by the property owner prepared by a professional engineer or environmental professional that is acceptable to the NYSDEC and complies with 6 NYCRR 375-1.8(h)(3) effective December 14, 2006. The certification is intended to validate that the institutional controls (and also engineering controls if required in the future) that are implemented for the Site are unchanged from the previous certification and that no circumstances have occurred that impair the ability of the controls to protect public health and the environment, or constitute a violation or failure to comply with any O&M or SMP for the Site.
- Development and implementation of an environmental easement to require compliance with the SMP; limit use of the Site to general commercial, industrial and passive recreational facilities; restrict use of groundwater as a source of potable water or process water, without necessary water quality treatment as determined by the NYSDOH; and require the property owner to complete and submit to the NYSDEC the annual certification described above. In addition, the NYSDEC will be given a 60-day notice in advance of any “change of use” at the Site.

3.5 Reporting

The results of the in-situ chemical oxidation work, and associated performance monitoring will be provided in an OU1 remediation/final engineering report (OU1 R/FER) for operable unit OU1 that will be signed, sealed and certified by a New York State Professional Engineer in accordance with guidance and regulations applicable at the time the report is prepared. The report will include: a summary of the work performed; figures showing well locations, injector locations, potentiometric groundwater contours, etc.; as-built drawings for the injection system(s); actual dosage rates for each location; approximate quantities and concentration of contaminants removed or treated; an identification and explanation for any deviations from the design plan(s); a description of any problems encountered and their resolution; a description of the effectiveness of the remedy including comparisons to RAOs; any waste stream and disposal documentation; selected photographs; boring logs; analytical laboratory data and associated chain-of-custody documentation; tables for baseline and performance monitoring data; and other pertinent information that is considered appropriate for inclusion. It is anticipated that at least the first year of post-treatment O&M groundwater monitoring will be included in the OU1 remediation report. The SMP and environmental easement will also be included as part of the OU1 R/FER.

Annual site management reports (SMRs) will be used to present subsequent post-treatment O&M groundwater monitoring events. Post-treatment O&M groundwater monitoring data in each annual SMR will include: applicable groundwater potentiometric maps; well sampling logs; analytical laboratory data and associated chain-of-custody documentation; data tables showing well elevations, static water levels, and calculated water elevations; and data tables showing cumulative groundwater testing results compared to applicable SCGs. Annual SMRs will also include the annual certification report, information and requirements set forth in Section 6.4(d) of DER-10 (or current version at the time the SMR is prepared) that pertain to the selected remedy and have not been presented in the FER or previous SMRs, and other pertinent information deemed necessary to evaluate the performance of the remedy. Details concerning the content of annual SMRs will be identified in the reporting plan section of the SMP.

Monthly progress reports for the Site will also include information pertaining to further development and implementation of the OU1 remedy as the project progresses.

3.6 Assessment of Selected Remedy

Protection of Human Health and the Environment: It is anticipated that the selected remedy (Baseline Groundwater Monitoring, In-Situ Chemical Oxidation of the On-Site Source Area, Post-Treatment Groundwater Monitoring, Institutional Controls) will be protective of human health and the environment under current site conditions and future use as general commercial, industrial and passive recreational facilities. Risks associated with potential human health exposure pathways will be eliminated or adequately controlled. With the exception of restoring the groundwater aquifer to pre-disposal/pre-release conditions, RAOs for soil and groundwater should be adequately addressed by this alternative in relation to protection of public health and the environment. The tasks associated with addressing the RAOs can readily be completed and should satisfy project objectives.

A potential challenge regarding human health and the environment is that artesian conditions are possible with Fenton’s reagent. This could result in safety concerns associated with this condition as well as the potential for contaminated groundwater and/or oxidant to migrate aboveground. Groundwater mounding may likely occur; however, by adjusting injection rates and reagent formulation coupled with other engineering controls, it is anticipated that little or no fluid will come to the surface. GCI will provide a health and safety plan that includes procedures for cleaning up spills of mounded fluid and reagents. Regulatory agency approval of the GCI health and safety plan will be mandatory prior to conducting any in-situ chemical oxidation applications.

Compliance with SCGs: It is anticipated that the selected remedy will result in an 80% to 90% reduction of contamination in soil and groundwater within the area that is treated. It is possible that exceedances of chemical-specific SCGs for soil and/or groundwater may exist subsequent to the chemical oxidation treatment; however, it is anticipated that the selected remedy will provide adequate monitoring of the natural attenuation of residual contamination in order to evaluate compliance trends in relation to chemical-specific SCGs. Location-specific SCGs are met since the institutional controls will be protective of human health and the environment. Action-specific SCGs should also be adequately addressed for this alternative.

Long-Term Effectiveness and Permanence: The long-term risk associated with the contamination will be permanently reduced by the in-situ chemical oxidation remediation and institutional controls that are to be implemented. It is anticipated that the selected remedy will prove to be reliable, and will have the ability to continue to meet RAOs in the future. The in-situ chemical oxidation is effective in the long term and permanently destroys the VOC and petroleum constituents. The long-term effectiveness and permanence of this alternative in relation to residual contaminants will be monitored.

A potential challenge regarding long-term effectiveness for this remedy is that oxygen generated by Fenton's reagent may become entrapped and interfere with groundwater transport and the delivery of hydrogen peroxide. This may result in poor mass transfer between aqueous, DNAPL and solid phases that could lead to contaminant rebound. However, gas blockage can, and is, controlled through GCI's use of stabilizers injected with the peroxide. A site-specific catalyst/stabilizer package is designed to prevent the rapid decomposition of the peroxide; thus, preventing gas blockage. The oxygen generated by the Fenton's reagent reaction will follow the path of least resistance to the surface either through pore spaces or through adjacent injector locations or monitoring wells. As indicated in Sections 3.1.1 and 3.1.2, a venting system (i.e., 16 vent wells) will be installed and utilized by GCO to further relieve gas buildup in the subsurface. The venting system will help to direct the flow of the generated gases to the surface, preventing any potential pore space blockage. This venting system will be incorporated into the current design by coupling the installation of the injectors with the installation of a venting system.

Also, a potential challenge regarding long-term effectiveness for this remedy is that formation of MnO_2(s) during permanganate oxidation can lead to permeability reductions, limited mass transfer, and rebound. GCI has indicated that this condition only occurs when large quantities of permanganate are injected. Since this treatment program is designed to use permanganate as a polishing agent and the overall chemical quantities are low, significant permeability reductions associated with formation of MnO_2(s) are not anticipated.

Another potential challenge regarding long-term effectiveness for this remedy is that injection of high concentrations of sodium-based oxidants (such as sodium permanganate) in clay-rich environments may be associated with permeability reductions. GCI has indicated that this condition only occurs in certain types of clay and would only present itself if large quantities of sodium permanganate were injected. Since this treatment program is designed to use permanganate as a polishing agent and the overall chemical quantities are low, significant permeability reductions associated with use of sodium permanganate in potentially clay-rich soils at this Site is not anticipated.

Reduction of Toxicity, Mobility and Volume: The in-situ chemical oxidation, natural attenuation and other factors such as advection, dispersion, sorption, diffusion, etc. that are occurring at this Site will result in a significant reduction of contaminant toxicity, mobility, and volume. The in-situ chemical oxidation is anticipated to result in an 80% to 90% reduction of contaminants within the area that is treated.

A potential challenge regarding mobility of contaminants for this remedy is that pressure build-up of oxygen created by Fenton's reagent could transport contaminated groundwater and DNAPL away from the treatment area and could potentially create artesian conditions at nearby monitoring/recovery wells, etc. However, GCI has indicated that this condition has not been found to occur. During many other projects, sentinel wells in "clean zones" were monitored to evaluate this condition. Peroxide in the system prevents contaminant migration. If groundwater mounding occurs as a result of the generation of off-gas, this situation is mitigated by GCI via a number of injection controls. Each injector is fitted with a ball-valve capable of withstanding the concentration of the injected reagents and the mild pressures generated as a result of the injection. The ball-valves can either be adjusted to allow the flow of gases only, or fitted with tubing and connected to a vessel designed to collect water or DNAPL. In addition, other measures such as perimeter injection create an oxidative barrier at the perimeter of the treatment area. As such, any material that may migrate from the treatment area would travel through an oxidizing solution.

Also, a potential challenge regarding mobility of contaminants for this remedy is that groundwater displacement during permanganate injection may lead to transport of groundwater and DNAPL away from the treatment area. However, it is estimated that DNAPL destruction will occur during the Fenton's reagent injection. The permanganate injection will focus on remaining dissolved phase constituents. In addition, permanganate is readily dissolved in groundwater, creating a permanganate solution that will remain reactive in the subsurface for longer periods of time (i.e., greater than three months). This reactive solution will continue to oxidize sorbed and dissolved phase constituents until the permanganate is no longer present. Perimeter injection will also be conducted initially with the permanganate solution.

Another potential challenge regarding mobility of contaminants for this remedy is that excessive heat generated by Fenton's reagent can result in steam formation, PVC well damage, contaminant volatilization (especially through nearby wells), and DNAPL transport. The exothermic nature of Fenton's reagent can cause an increase in groundwater temperatures, but will not cause the groundwater to boil. The greatest temperature increases typically occur at the injector locations themselves, as that is where the highest concentrations of oxidant (between 3% and 12%) are delivered. Typical increases in temperature are between approximately 10 to 20° F. Oxidant concentrations are much lower in the monitoring wells (less than 1%); thus, the monitoring wells will experience less exothermic effect. GCI has indicated that the 0.75-inch inner diameter Schedule 80 CPVC injector materials specified for use on this project have been proven to be able to handle the mild pressures and slight temperature increases that can occur as a result of the oxidation reaction.

Another potential challenge regarding mobility of contaminants for this remedy is that chemical oxidation using Fenton's reagent and permanganate can result in increased concentration and transport of metals. Due to the temporary shift of pH that occurs during a Fenton's reagent in-situ chemical oxidation treatment program (between 4-6), metal concentrations in groundwater can temporarily increase. This condition is readily remedied once the aquifer returns to ambient conditions. If deemed necessary, GCI can inject caustic reagents once the oxidant has dissipated to return the groundwater pH to ambient conditions; thus, precipitating any dissolved metals. Sodium permanganate also contains trace metals that may slightly increase metals concentrations in groundwater. However, this condition only occurs when large quantities of permanganate are injected. The treatment program for the Site is designed to use permanganate as a polishing agent; thus, the overall chemical quantities are low.

Short-Term Impacts and Effectiveness: The selected remedy will likely result in a slight risk in regard to short-term impacts. It is anticipated that Site remediation workers will have an increased potential to be exposed to Site contamination and treatment chemicals associated with the Fenton's reagent during the in-situ chemical oxidation work. It is also anticipated that Site remediation workers will have an increased potential to be exposed to residual Site contamination during long-term groundwater monitoring. Implementation of the SMP and HASP provisions should protect site remediation workers from these short-term risks. It is anticipated that this alternative will not increase short-term risks to occupants of the Site or the surrounding community.

A potential challenge regarding short-term impacts for this remedy is the potential for permanganate to migrate off-site to the wetland or the former ship channel via groundwater transport, migrate along buried storm sewer pipe, or migrate overland from spills/blowback during injection or artesian conditions that could occur during precipitation or snowmelt events. However, GCI has indicated that the potential for any of these situations to occur is low. Permanganate is going to be injected at concentrations between 0.1% and 4%. Upon dissolution into groundwater, permanganate concentrations will be much lower. The permanganate will then be consumed by any remaining contaminant mass, deposited as manganese dioxide, or consumed by background demand.

<u>Implementability:</u> The selected remedy can be implemented easily in relation to the current site conditions and anticipated future use as general commercial, industrial and passive recreational facilities. Spatial requirements are limited and would not impede completion of this remedy.

The presence of DNAPL is a potential challenge for implementing this remedy. However, DNAPL monitoring and recovery have been performed at the former plating pond/lagoon since July 30, 2003 as an interim remedial measure. Between July 30, 2003 and December 22, 2004, approximately 162 gallons of DNAPL were removed from recovery wells. Between January 7, 2005 and November 30, 2006, approximately 20 gallons of DNAPL have been removed from recovery wells. This data suggests free-phase DNAPL is being depleted at the former plating pond/lagoon. This DNAPL monitoring and recovery will continue until such time that the NYSDEC concurs that it can be terminated.

A potential challenge regarding implementing this remedy is that acidification of the treatment zone needed for Fenton's reagent may be difficult if the groundwater is well buffered. During the injector installation phase of both the Pilot Phase and the Full-Scale Phase (primary) in-situ chemical oxidation treatment programs, GCI collects soil cores from the lithologies within, above and below, (as applicable) and tests their buffering capacities. GCI uses the results from these tests to formulate a site-specific catalyst capable of addressing any potential issues associated with soil buffering. Unless the site is in reactive limestone (which is not the case for this Site), the injectate can be formulated to create effective oxidizing conditions. To be effective, only a temporary, slightly acidic (pH ~5) groundwater condition needs to be established in the subsurface.

Another potential challenge regarding implementing this remedy is that hydraulic short-circuiting and preferential pathways can result in uneven dispersion of the oxidant in the treatment area and lower overall treatment effectiveness. This may be of particular concern if injecting near the more permeable interface between native soil and the backfill within the footprint of the former plating pond/lagoon. GCI utilizes several injection methodologies that can overcome these types of situations:

- Injectors are installed on an approximate 15-ft grid, with a radius of 7.5 ft, with a 2.5 ft overlap.

- GCI can inject at multiple injection locations simultaneously, allowing the fluid static pressures to force reagents into less permeable formations.
- GCI can isolate portions of the injection screen using a specialized injection procedure proven to be effective to deliver reagents into adjacent low permeability areas. This technique may prove useful in the area of the former plating pond lagoon that was backfilled with more permeable fill and is underlain by less permeable native soil.
- Off-gas and exothermic reaction can also enhance reagent permeation into tighter lithologies.

In summary, the use of Fenton's reagent and sodium permanganate for in-situ chemical oxidation at this Site is a desirable remedy for addressing the contamination associated with operable unit OU1. Potential challenges may exist; however, viable solutions have been identified. These solutions will be considered when developing the associated remedial design plans and implementing the remedy for operable unit OU1.

Planned Future Use of the Site: Based on the findings of studies performed to date, it is anticipated that the selected remedy will be acceptable in relation to the current use of the Site, and also the anticipated future use of the Site as general commercial, industrial and passive recreational facilities.

Cost: An opinion of probable costs for the selected remedy is summarized below and presented in more detail in Table 1 included in Appendix A.

Total Present Worth	$ 1,045,096
Capital/Initial Cost	$ 890,400
O&M/Annual/Closeout Present Worth Cost	$ 154,696

The opinion of probable cost that is provided is dependent upon numerous assumptions and factors. As a result, the actual cost associated with the selected remedy may vary from the opinion of probable cost that is provided.

Community Acceptance: It is anticipated that the selected remedy will be acceptable to the community, and that any public comments, concerns or overall perception can be adequately addressed.

4.0 PRELIMINARY SCHEDULE

This preliminary schedule provides an estimate of the amount of time it would take to complete key tasks associated with the OU1 Remedial Work Plan. This preliminary schedule assumes that NYSDEC approval of the OU1 Remedial Work Plan would be obtained in the spring of the year 2007. A detailed schedule can be developed once the OU1 Remedial Work Plan is formally approved by the NYSDEC.

- It is anticipated that the remedial design investigation could be started within one month of NYSDEC approval of the OU1 Remedial Work Plan, and that the remedial design investigation results would be available within three months of the date this task is started.
- Assuming regulatory approval is obtained in the spring of the year 2007, the remedial tasks could be started in the spring of 2007. Development and subsequent NYSDEC approval of the Pilot Phase Remedial Design Plan would take about five months to complete. The Pilot Phase field activities (using both Fenton's reagent and sodium permanganate) would take four or more months to complete. Development and subsequent NYSDEC approval of a Pilot Phase Report and Full-Scale Phase Remedial Design Plan would take about six months to complete. The Full-Scale Phase field activities would take three or more months to complete. If deemed necessary subsequent to evaluating Full-Scale Phase performance monitoring results, development and subsequent NYSDEC approval of a Polishing Phase Remedial Design Plan would take about five months to complete. It is anticipated that the Polishing Phase would take two or more months to complete. As such, the in-situ chemical oxidation activities would take a total of twenty-five or more months to complete.
- Post-treatment O&M groundwater monitoring could be started within six months after completing the in-situ chemical oxidation activities, and would continue for up to five years.
- Remediation-derived wastes would be disposed as they are generated in accordance with applicable regulations.
- The institutional controls would be completed within approximately two months after completing the in-situ chemical oxidation activities.
- The OU1 R/FER could be developed within six months after completing the in-situ chemical oxidation activities.

5.0 HEALTH AND SAFETY

The site-specific Health and Safety Plan (HASP) dated November 2001, which was included as part of the General Investigation Work Plan dated June 2002 would be implemented during performance of the tasks presented in this OU1 Remedial Work Plan. The HASP includes a community air monitoring program (CAMP). As an exception, the radiation monitoring identified in the HASP would not be conducted since previous monitoring in the OU1 area did not identify radiation measurements of concern. In addition, DAY or GCI (or a similar contractor) would provide a separate HASP to be implemented during activities that are associated with the in-situ chemical oxidation treatments and performance monitoring events.

6.0 QUALITY ASSURANCE/QUALITY CONTROL

The applicable quality assurance/quality control (QA/QC) protocols and procedures included in Section 5.0 of the General Investigation Work Plan dated June 2002 would be implemented during performance of the tasks presented in this OU1 Remedial Work Plan. This includes performing a Data Usability Summary Report (DUSR) on some of the analytical laboratory data that is generated as part of the scope-of-work in this OU1 Remedial Work Plan, to the extent required by the NYSDEC (e.g., post-treatment Full-Scale Phase confirmatory soil samples, and one or more groundwater monitoring events).

7.0 REFERENCES

Project Documents

Voluntary Cleanup Agreement Index #B8-590-01-02 executed by NYSDEC July 13, 2001.

General Investigation Work Plan, June 2002.

Health and Safety Plan, November 2001

Previous Reports

Former Air Force Plant No. 51, Monroe County, Greece, New York, Interim Removal Action Area 1, Final Completion Report; August 2001; Roy F. Weston, Inc.

Environmental Site Investigation Report; Former Air Force Plant 51; 4777 Dewey Avenue, Greece, New York; DERP-FUDS Site No. C02NY057500; NYSDEC Site No. V00421; Operable Unit OU1; AOC1 (Former Plating Pond/Lagoon); AOC2 (Lagoon and Stormwater Outfalls); April 3, 2006; Day Environmental, Inc.

Regulatory Documents

NYSDEC Division of Water Technical and Operational Guidance Series 1.1.1 document titled "Ambient Water Quality Standards and Guidance Values and Groundwater Effluent Limitations" (TOGS 1.1.1) dated June 1998, including April 2000 Addendum Table 1.

NYSDEC Division of Technical and Administrative Guidance Memorandum, Determination of Soil Cleanup Objectives and Cleanup Levels (TAGM 4046) dated January 24, 1994, as amended by Memorandums dated December 20, 2000, April 10, 2001, and July 10, 2001.

NYSDEC Draft DER-10 Technical Guidance for Site Investigation and Remediation, December 2002.

NYSDEC 6 NYCRR Part 375 Environmental Remediation Program; revised December 14, 2006.

USEPA August 2006 Engineering Issue, “In-Situ Chemical Oxidation” S.G. Huling and B.E. Pivetz, EPA/600/R-06/072

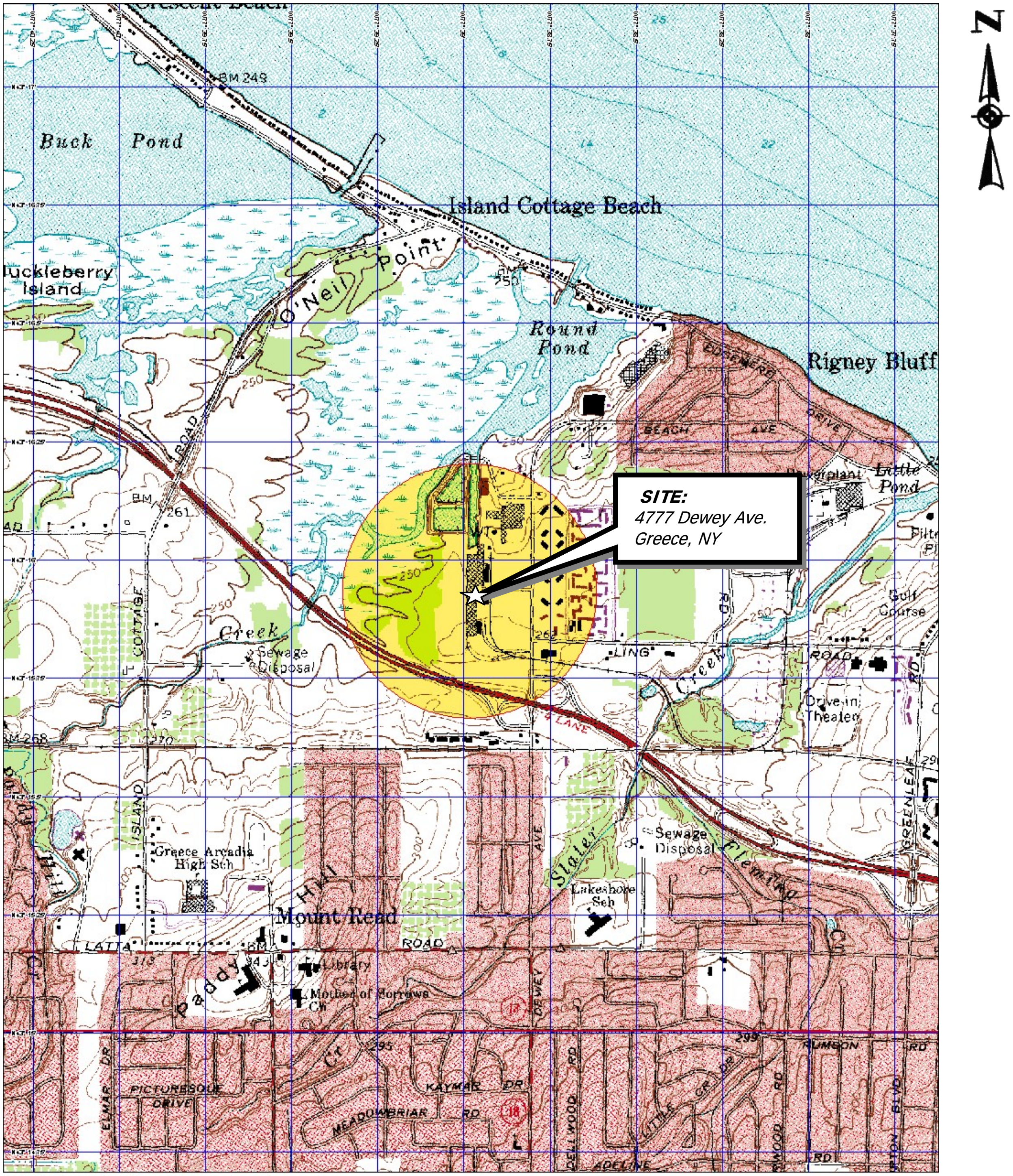
Other Reference Materials

USGS topographic map for the Braddock Heights, New York quadrangle, 1995.

8.0 ACRONYMS

AFP51	Air Force Plant No. 51
AOC	Area of Concern
ASP	Analytical Services Protocol
CAMP	Community Air Monitoring Program
CPVC	Chlorinated Polyvinyl Chloride
4800 Dewey	4800 Dewey Avenue, Inc.
DNAPL	Dense Non-Aqueous Phase Liquid
DUSR	Data Usability Summary Report
ELAP	Environmental Laboratory Approval Program
GCI	Geo-Cleanse International, Inc.
GSA	General Services Administration
HASP	Health and Safety Plan
IRM	Interim Remedial Measure
LNAPL	Light Non-Aqueous Phase Liquid
MCWA	Monroe County Water Authority
MS/MSD	Matrix Spike/Matrix Spike Duplicate
NTU	Nephelometric Turbidity Unit
NYCRR	New York Codes, Rules and Regulations
NYSDEC	New York State Department of Environmental Conservation
NYSDOH	New York State Department of Health
O&M	Operation and Maintenance
OU1	Operable Unit OU1
PCB	Polychlorinated Biphenyl
PID	Photoionization Detector
PVC	Polyvinyl Chloride
QA/QC	Quality Assurance/Quality Control
RAO	Remedial Action Objective
R/FER	Remediation/Final Engineering Report
RSCO	Recommended Soil Cleanup Objective
SCG	Standard, Criteria and Guidance
SCOs	Soil Cleanup Objectives
SMP	Site Management Plan
SMR	Site Management Report
SOQ	Statement of Qualifications
SVOC	Semi-Volatile Organic Compound
TAGM	Technical and Administrative Guidance Memorandum
TAL	Target Analyte List
TCL	Target Compound List
TOGS	Technical and Operational Guidance Series
VCA	Voluntary Cleanup Agreement
VOC	Volatile Organic Compound
USACE	United States Army Corps of Engineers
USEPA	United States Environmental Protection Agency
USGS	United States Geological Survey

FIGURES



3-D TopoQuads Copyright © 1999 DeLorme Yarmouth, ME 04096 Source Data: USGS

544 ft Scale: 1 : 19,200 Detail: 14-0 Datum: WGS84

Drawing Produced From: 3-D TopoQuads, DeLorme Map Co., referencing USGS quad maps Braddock Heights (NY) 1995 and Rochester East (NY) 1995. Site Lat/Long: N43d-15.94' – W77d-38.98'

DATE
9/12/2006

DRAWN BY
Tww

SCALE
1" = 2000'

day
DAY ENVIRONMENTAL, INC.
ENVIRONMENTAL CONSULTANTS
ROCHESTER, NEW YORK 14614-1008

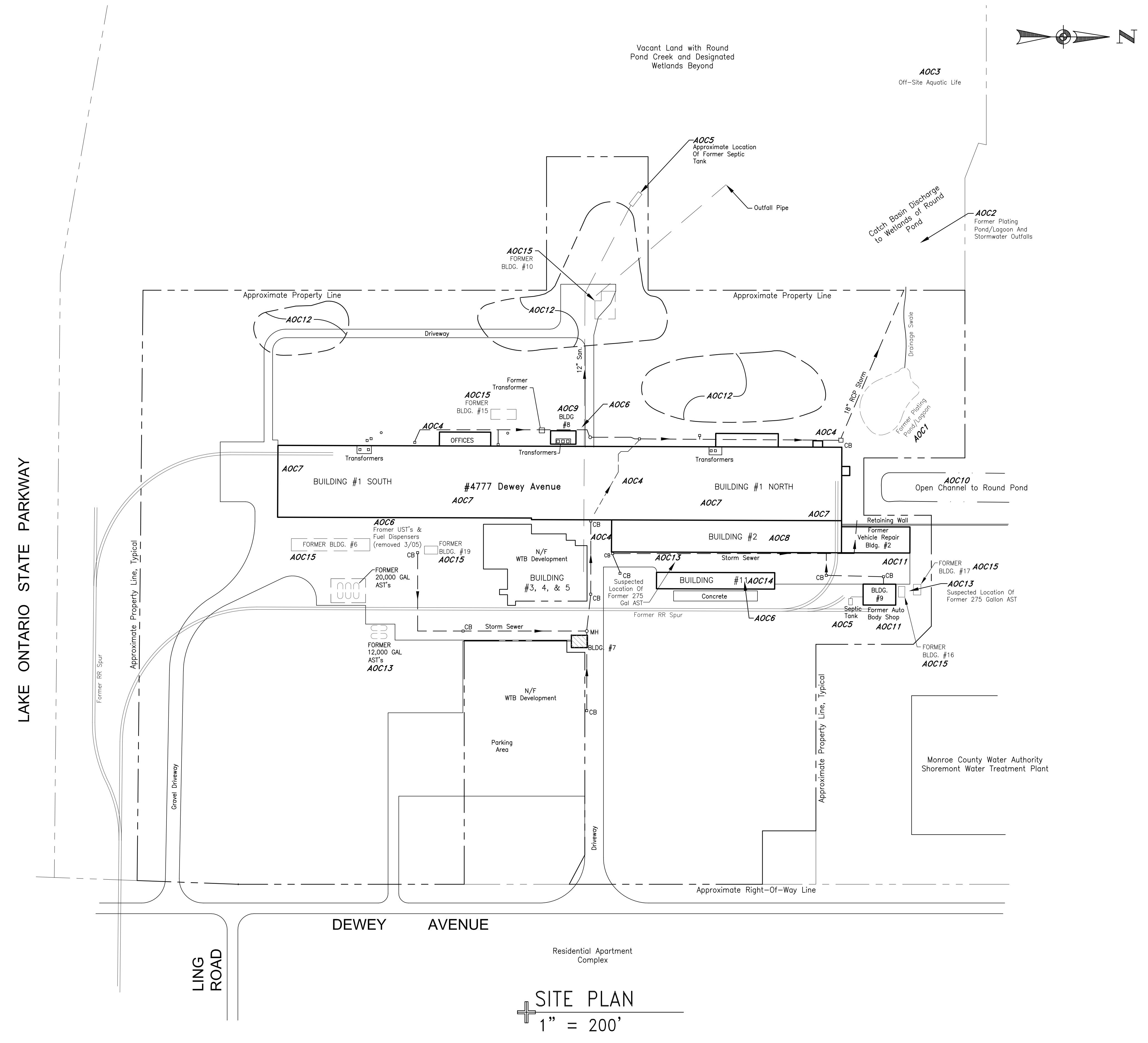
PROJECT TITLE
4777 DEWEY AVENUE
GREECE, NEW YORK

OU1 REMEDIAL WORK PLAN

DRAWING TITLE
PROJECT LOCUS MAP

PROJECT NO.
2806S-01

Figure
AOC1-A



SITE PLAN
1" = 200'

LEGEND:

AOC12	Area of Concern with designation

LIST OF AREAS OF CONCERN (AOCs)

AOC1	Former Plating Pond/Lagoon
AOC2	Lagoon and Stormwater Outfalls
AOC3	Off–Site Aquatic Life
AOC4	Stormwater System
AOC5	Septic System
AOC6	Underground Storage Tank Systems
AOC7	Building #1
AOC8	Building #2
AOC9	Building #8 and Other Transformer Areas
AOC10	Shoremont Water Treatment Plant and Former Man–Made Channel
AOC11	Vehicle Repair Facilities
AOC12	Suspect Chemical Disposal Area and Other Areas of Suspect Dumping and Filling
AOC13	Aboveground Storage Tank System
AOC14	Building #11
AOC15	Demolished Buildings
AOC16	Miscellaneous Site Areas

NOTES:

1. Drawing prepared from: 1) A paper drawing by William M. Szawranskyj, P.E.,L.S., titled "Existing Water Disposal, Flower City Printing, Being Part Of Town Lot 44, Township 2, Short Range, Town Of Greece, Monroe County, NY" dated February 1987; 2) Monroe County Tax Map Number 046.01; 3) Various Figures from a report titled "Former Air Force Plant No. 51, HTRW Investigation, Greece, NY" by Ogden Environmental and Energy Services Co., Inc, dated April 2000; 4) A drawing for MCWA Water Treatment Plant by Metcalf & Eddy Engineers, Drawing Sheet A–1, "Architectural Plot Plan", date last revised 2–9–62; 5) Figure by Neil Norry, PO Box 51, Rochester, NY, CL–4–9058; 6) A paper drawing titled "Final Plans For Ext. 313 To Sewer Dist. 1", dated May 26, 1987; 7) Site observations by representatives of Day Environmental, Inc during November 2001 through November 2004.

FIELD VERIFIED BY	JAD
DATE	09-2006
DRAWN BY	RJM
DATE DRAWN	09-13-2006
SCALE	1" = 200'
DATE ISSUED	09-19-2006

day
DAY ENVIRONMENTAL, INC.
ENVIRONMENTAL CONSULTANTS
ROCHESTER, NEW YORK 14614-1008
NEW YORK, NEW YORK 10165-1617

PROJECT TITLE
4777 DEWEY AVENUE
GREECE, NEW YORK

OU1 REMEDIAL WORK PLAN

DRAWING TITLE
Site Plan

PROJECT NO.
2806S-01

AOC1-B

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Ref5:
Ref6:

Ref1:
Ref2:
Ref3:

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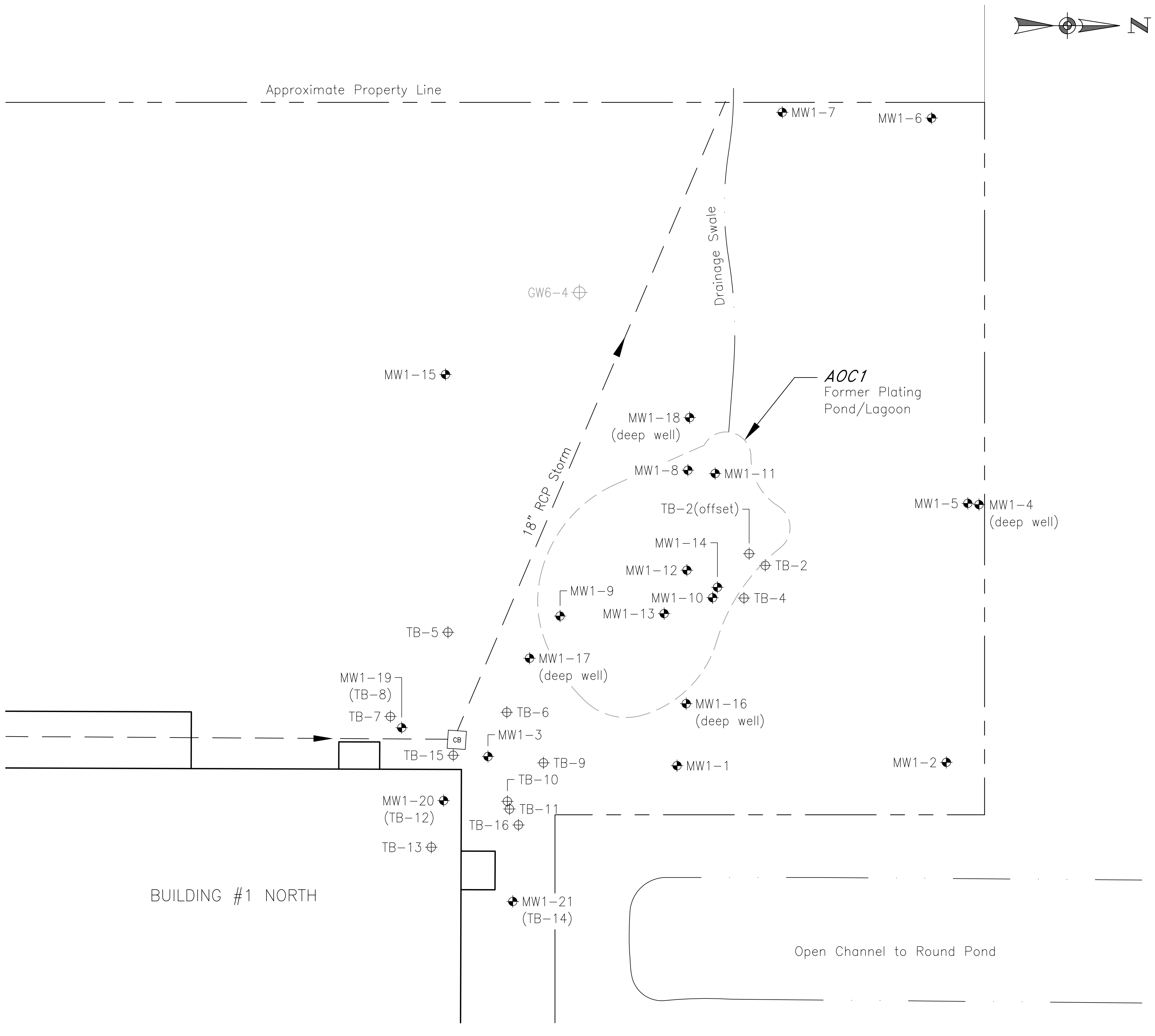

Test Location Plan
1" = 50'

NOTES:

1. Monitoring Well MW1−1 thru MW1−10 are 2" PVC wells installed December 2002.
2. Monitoring Wells MW1−11 thru MW1−14 are 4" Stainless Steel wells installed July 2003.
3. Monitoring Well MW1−15 thru MW1−21 are 2" PVC wells installed March 2004.
4. Drawing prepared from Figure GEN−2 in the general work plan dated June 2002 and site observations by representatives of Day Environmental, Inc. from December 2002 through April 2004.

LEGEND:

⊕ GW6−4	Well Location identified from a report titled "Former Air Force Plant No. 51, HTRW Investigation, Greece, NY" by Ogden Environmental And Energy Services Co., Inc, dated April 2000
AOC1	Area Of Concern with Numbered Designation
◈ MW1−1	Monitoring Well with Designation
⊕ TB−2	Test Boring with Designation

DATE	09-2006
FIELD VERIFIED BY	JAD
DATE DRAWN	09-13-2006
DRAWN BY	RJM
DATE ISSUED	09-19-2006
SCALE	1" = 50'

DAY ENVIRONMENTAL, INC.
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ROCHESTER, NEW YORK 14614-1008
NEW YORK, NEW YORK 10165-1617

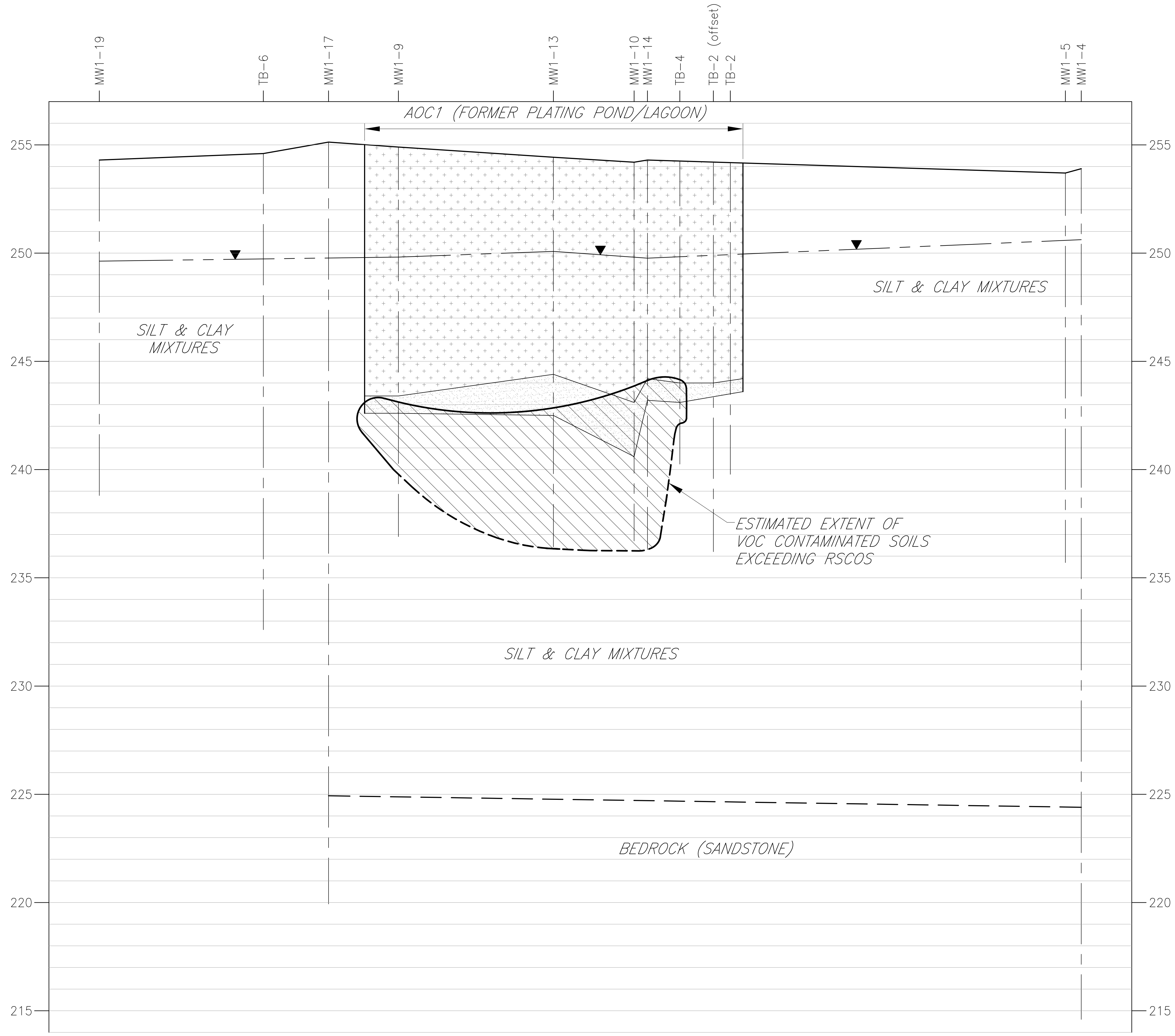
PROJECT TITLE
4777 DEWEY AVENUE
GREECE, NEW YORK

OU1 REMEDIAL WORK PLAN

DRAWING TITLE
Previous Test Locations Plan

PROJECT NO.
2806S-01

AOC1-C



GEOLOGIC CROSS-SECTION A-A'

1" = 30' Horizontal
1" = 5' Vertical

LEGEND

⁘	FILL (SILT)
░	FILL (SAND)
▨	ESTIMATED EXTENT OF VOC CONTAMINATED SOILS EXCEEDING RECOMMENDED SOIL CLEANUP OBJECTIVES (RSCOS) EXTENT IS INFERRED WHERE DASHED
—▼—	INFERRED GROUNDWATER ELEVATIONS BASED ON STATIC WATER LEVEL MEASUREMENTS COLLECTED FROM SHALLOW OVERBURDEN MONITORING WELLS ON AUGUST 30, 2004

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Ref2:
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Ref4:
Ref5:
Ref6:

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Layout Name: Layout 1

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FIELD VERIFIED BY **JAD**	DATE **01-2007**
DRAWN BY **RJM**	DATE DRAWN **01-17-2007**
SCALE **As Noted**	DATE ISSUED **01-17-2007**

day
DAY ENVIRONMENTAL, INC.
ENVIRONMENTAL CONSULTANTS
ROCHESTER, NEW YORK 14614-1008
NEW YORK, NEW YORK 10165-1617

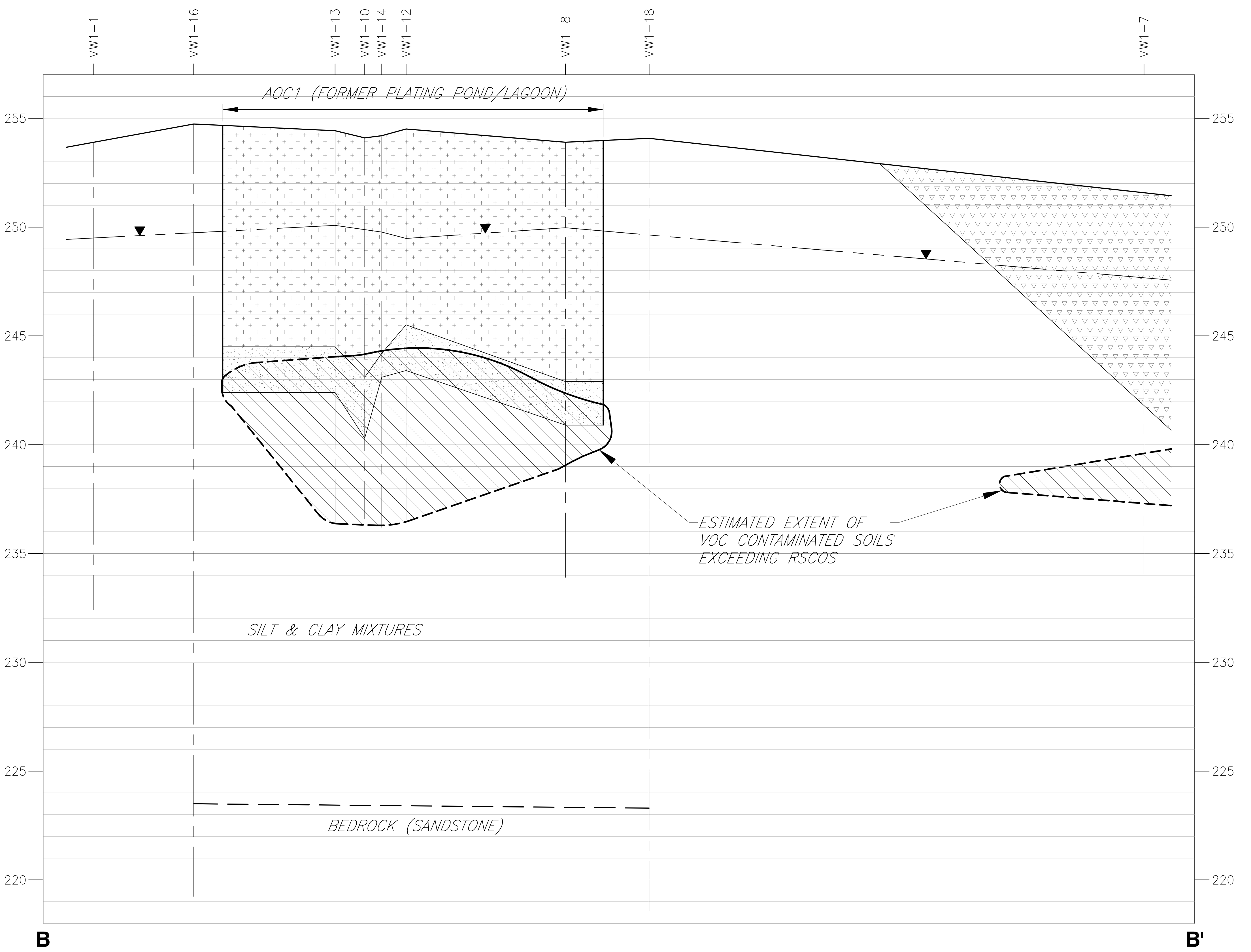
PROJECT TITLE
4777 DEWEY AVENUE
GREECE, NEW YORK

OU1 REMEDIAL WORK PLAN

DRAWING TITLE
Cross-Section A-A'

PROJECT NO.
2806S-01

AOC1-D



GEOLOGIC CROSS-SECTION B-B'

1" = 30' Horizontal
1" = 5' Vertical

LEGEND

- ▽ FILL (REWORKED SOIL BURNED WOOD)
- ⁺ FILL (SILT)
- ░ FILL (SAND)
- ▨ ESTIMATED EXTENT OF VOC CONTAMINATED SOILS EXCEEDING RECOMMENDED SOIL CLEANUP OBJECTIVES (RSCOS) EXTENT IS INFERRED WHERE DASHED
- ▼ INFERRED GROUNDWATER ELEVATIONS BASED ON STATIC WATER LEVEL MEASUREMENTS COLLECTED FROM SHALLOW OVERBURDEN MONITORING WELLS ON AUGUST 30, 2004

Ref1: Section B_BRevised.dwg
Ref2:
Ref3:
Ref4:
Ref5:
Ref6:

Xerox432AnsiB-2; 11 x 17
Layout Name: Layout 1

Time Plotted: Wed Jan 17 13:30 2007
File Name: Atkin\4800 Dewey\2806\2806-35RWP.dwg

FIELD VERIFIED BY JAD	DATE 01-2007
DRAWN BY RJM	DATE DRAWN 01-17-2007
SCALE As Noted	DATE ISSUED 01-17-2007

DAY ENVIRONMENTAL, INC.
ENVIRONMENTAL CONSULTANTS
ROCHESTER, NEW YORK 14614-1008
NEW YORK, NEW YORK 10165-1617

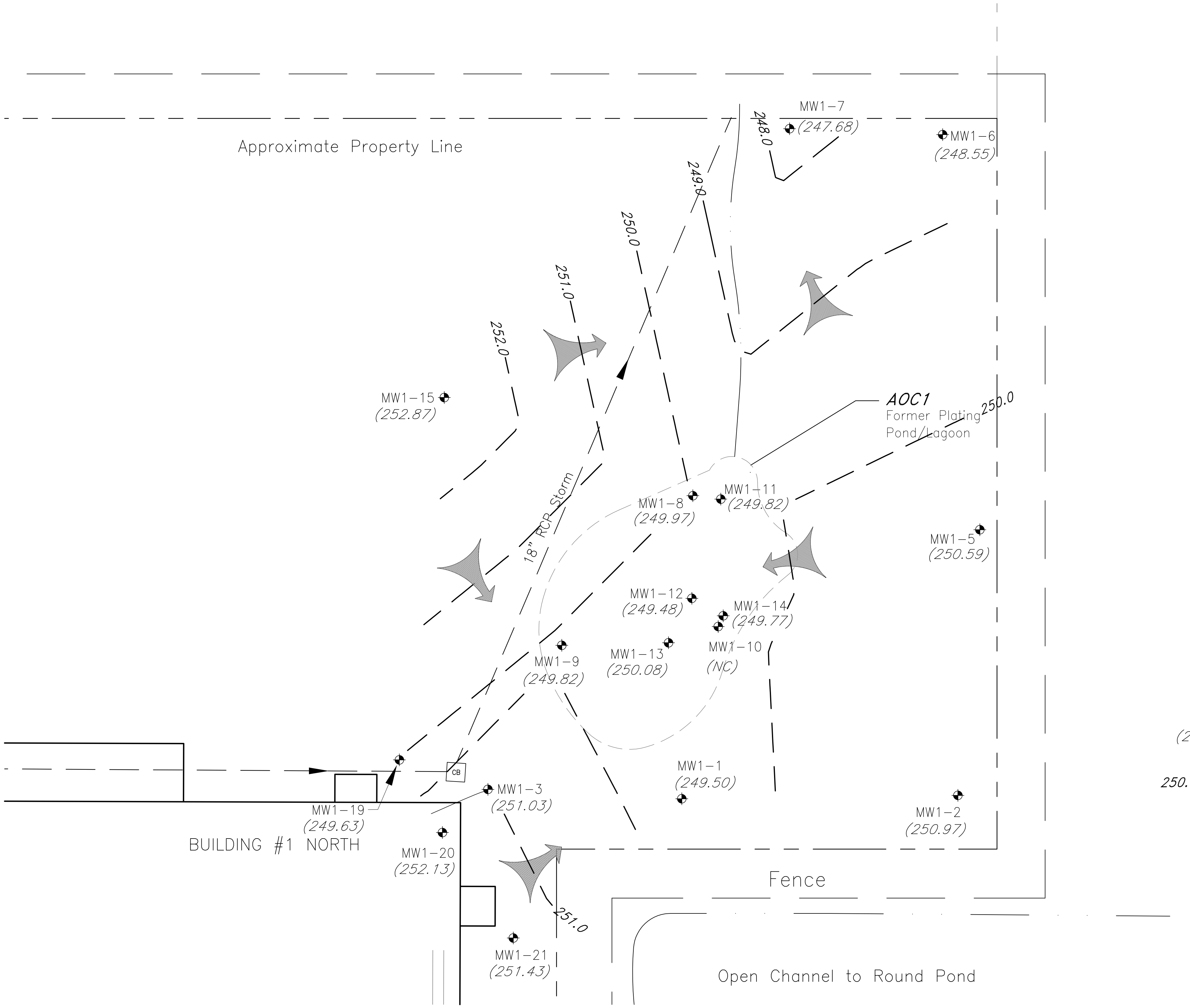
PROJECT TITLE
4777 DEWEY AVENUE
GREECE, NEW YORK

OU1 REMEDIAL WORK PLAN

DRAWING TITLE
Cross-Section B-B'

PROJECT NO.
2806S-01

AOC1-E



Test Location Plan
1" = 50'

NOTES:

1. Monitoring Well MW1−1 thru MW1−10 are 2" PVC wells installed December 2002.
2. Monitoring Wells MW1−11 thru MW1−14 are 4" Stainless Steel wells installed July 2003.
3. Monitoring Well MW1−15 thru MW1−18 are 2" PVC wells installed March 2004.
4. Drawing prepared from Figure GEN−2 in the general work plan dated June 2002 and site observations by representatives of Day Environmental, Inc. from December 2002 through April 2004.

LEGEND:

AOC1	Area Of Concern with numbered designation
MW1−7 ● (247.68)	Monitoring well with designation and groundwater elevation measured on August 30, 2004
250.00 — —	Potentiometric Contour Line
➜	Apparent Direction Of Groundwater Flow
(NC)	Measurement Not Collected

DesignTag JAD		DATE 01-2007
DRAWN BY RJM		DATE DRAWN 01-17-2007
SCALE 1"= 50'		DATE ISSUED 01-17-2007

day
DAY ENVIRONMENTAL, INC.
ENVIRONMENTAL CONSULTANTS
ROCHESTER, NEW YORK 14614-1008

PROJECT TITLE
4777 DEWEY AVENUE
GREECE, NEW YORK

OU1 REMEDIAL WORK PLAN

DRAWING TITLE
Potentiometric Overburden Groundwater Contour Map For August 30, 2004

PROJECT NO.
2806S-01

AOC1-F

Time Plotted: Wed Jan 17 13:55 2007
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Xerox432AnsiB-2; 11 x 17
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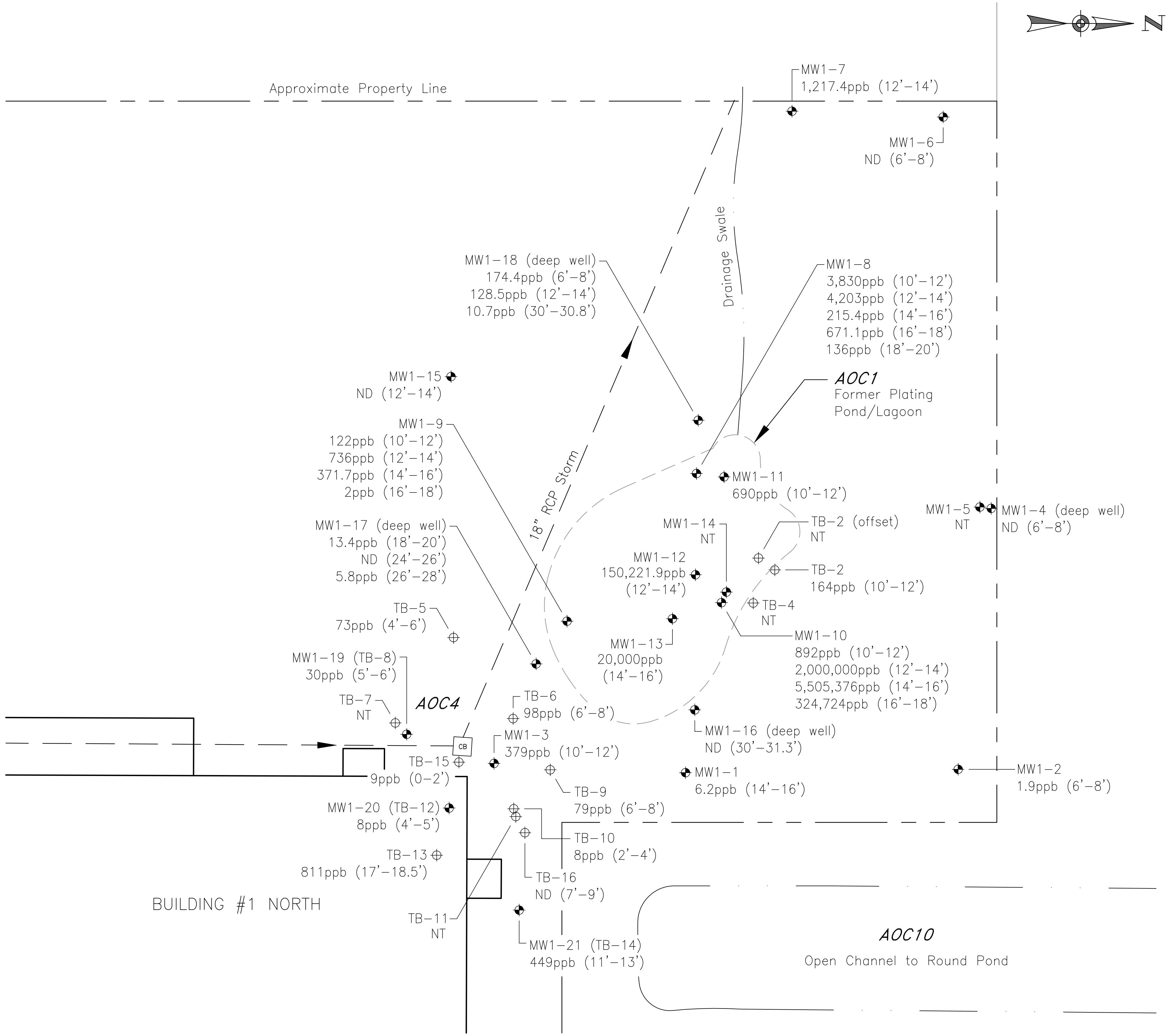
Ref2:
Ref3:
Ref4:
Ref5:
Ref6:



Test Location Plan

1" = 50'

NOTES:

1. Monitoring Well MW1−1 thru MW1−10 are 2" PVC wells installed December 2002.
2. Monitoring Wells MW1−11 thru MW1−14 are 4" Stainless Steel wells installed July 2003.
3. Monitoring Well MW1−15 thru MW1−21 are 2" PVC wells installed March 2004.
4. Drawing prepared from Figure GEN−2 in the general work plan dated June 2002 and site observations by representatives of Day Environmental, Inc. from December 2002 through April 2004.

LEGEND:

AOC1	Area Of Concern with Numbered Designation
◆ MW1−1	Monitoring Well with Designation
⊕ TB−2	Test Boring with Designation
6.2ppb (14'−16')	Total VOCs detected in parts per billion (ppb) from depth interval in parenthesis
ND	Not detected at concentration above reported analytical laboratory dectection limit
NT	Not tested

FIELD VERIFIED BY **JAD**	DATE **01-2007**
DRAWN BY **RJM**	DATE DRAWN **01-17-2007**
SCALE **1" = 50'**	DATE ISSUED **01-17-2007**

DAY ENVIRONMENTAL, INC.
ENVIRONMENTAL CONSULTANTS
ROCHESTER, NEW YORK 14614-1008
NEW YORK, NEW YORK 10165-1617

PROJECT TITLE
4777 DEWEY AVENUE
GREECE, NEW YORK

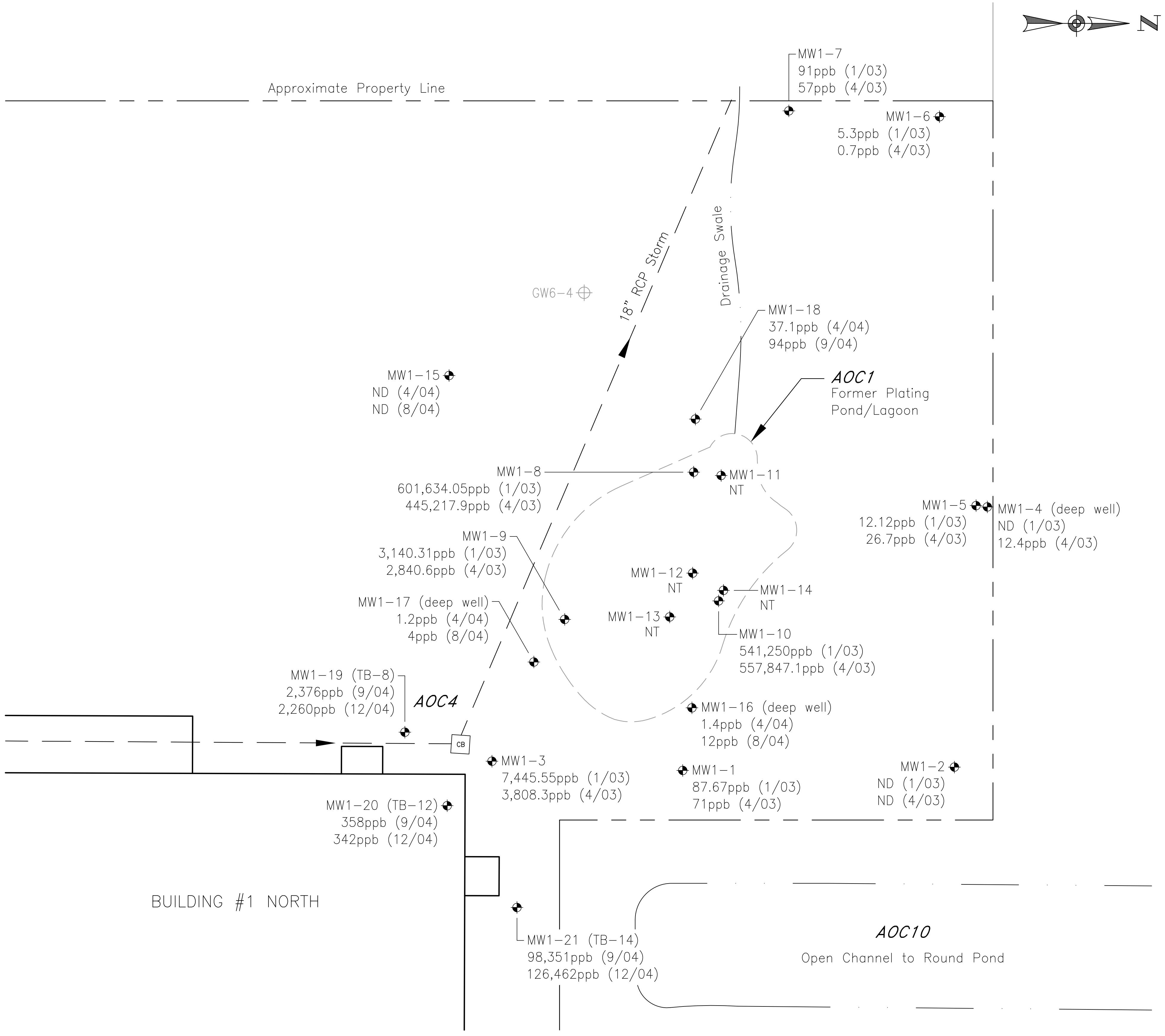
OU1 REMEDIAL WORK PLAN

DRAWING TITLE
Total VOCs In Soil

PROJECT NO.
2806S-01

AOC1-G

Time Plotted: Wed Jan 17 14:10 2007
File Name: Atkin\4800 Dewey\2806\2806-38RWP.dwg
Xerox432AnsiB-2; 11 x 17
Layout Name: Layout 1
Pen Setting File:
Ref1:
Ref2:
Ref3:



Test Location Plan

1" = 50'

NOTES:

1. Monitoring Well MW1−1 thru MW1−10 are 2" PVC wells installed December 2002.
2. Monitoring Wells MW1−11 thru MW1−14 are 4" Stainless Steel wells installed July 2003.
3. Monitoring Well MW1−15 thru MW1−21 are 2" PVC wells installed March 2004.
4. Drawing prepared from Figure GEN−2 in the general work plan dated June 2002 and site observations by representatives of Day Environmental, Inc. from December 2002 through April 2004.

LEGEND:

⊕ GW6−4	Well Location identified from a report titled "Former Air Force Plant No. 51, HTRW Investigation, Greece, NY" by Ogden Environmental And Energy Services Co., Inc., dated April 2000
AOC1	Area Of Concern with Numbered Designation
⊕ MW1−1	Monitoring Well with Designation
⊕ TB−2	Test Boring with Designation
87.67ppb (1/03)	Total VOCs detected in parts per billion (ppb) in groundwater sample collected in month/year in parenthesis
ND	Not detected at concentration above reported analytical laboratory dectection limit
NT	Not tested

DATE	01-2007
FIELD VERIFIED BY	JAD
DATE DRAWN	01-17-2007
DRAWN BY	RJM
DATE ISSUED	01-17-2007
SCALE	1" = 50'

day
DAY ENVIRONMENTAL, INC.
ENVIRONMENTAL CONSULTANTS
ROCHESTER, NEW YORK 14614-1008
NEW YORK, NEW YORK 10165-1617

PROJECT TITLE
4777 DEWEY AVENUE
GREECE, NEW YORK

OU1 REMEDIAL WORK PLAN

DRAWING TITLE
Total VOCs In Groundwater

PROJECT NO.
2806S-01

AOC1-H

Time Plotted: Wed Jan 17 14:15 2007
File Name: Atkin\4800 Dewey\2806\2806−39.dwg

Xerox432AnsiB−2; 11 x 17
Layout Name: OU1 RWP

Ref1:
Ref2:
Ref3:

Ref4:
Ref5:
Ref6:

Ref4:
Ref5:
Ref6:

Ref1: TCL-GW.dwg
Ref2:
Ref3:

Xerox432AnsiB-2; 11 x 17
Layout Name: OU1 RWP

Time Plotted: Wed Jan 17 14:20 2007
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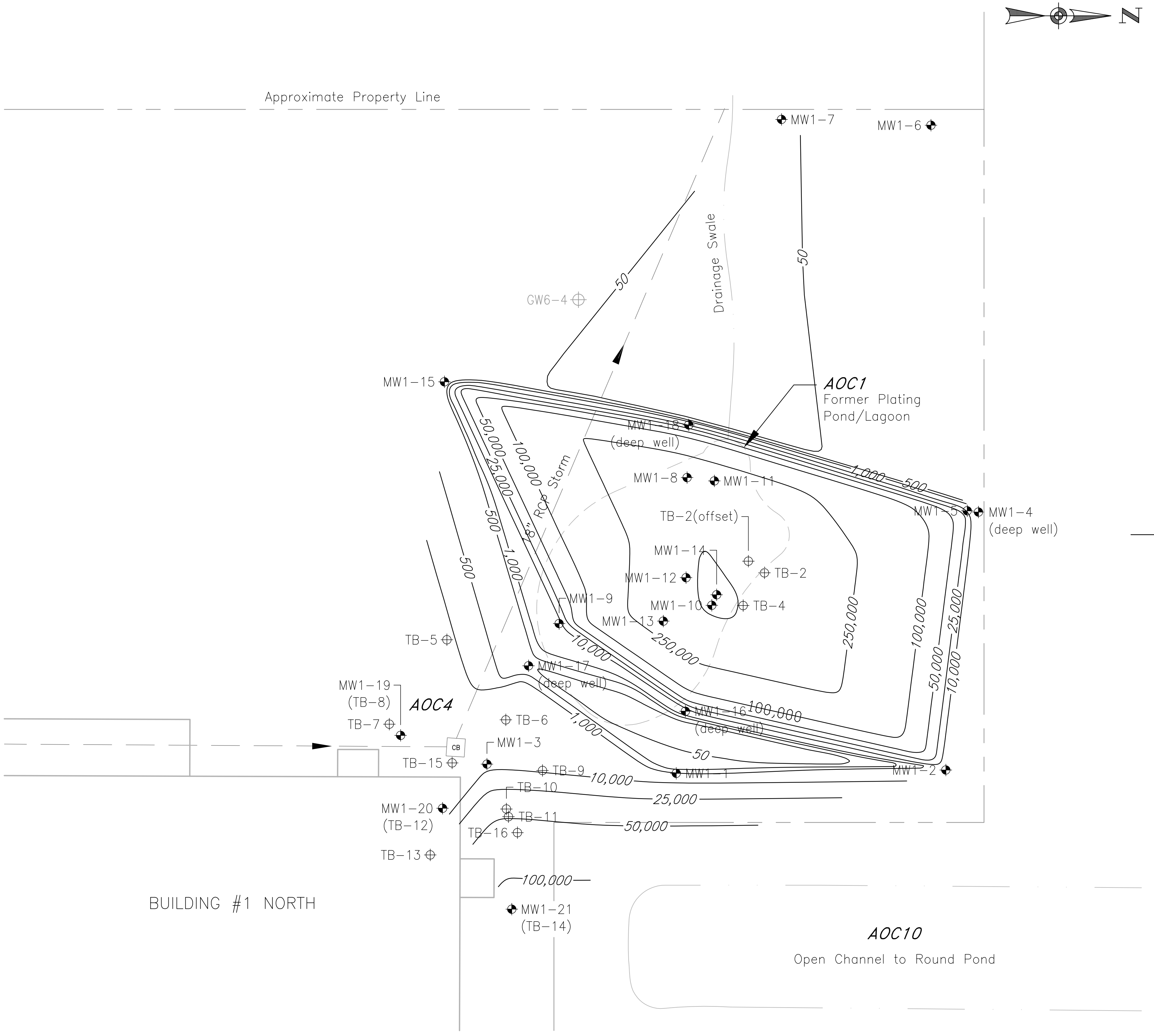


Total TCL VOCs & TICs in Groundwater Contour Map

1" = 50'

NOTES:

1. Monitoring Well MW1-1 thru MW1-10 are 2" PVC wells installed December 2002.
2. Monitoring Wells MW1-11 thru MW1-14 are 4" Stainless Steel wells installed July 2003.
3. Monitoring Well MW1-15 thru MW1-21 are 2" PVC wells installed March 2004.
4. Drawing prepared from Figure GEN-2 in the general work plan dated June 2002 and site observations by representatives of Day Environmental, Inc. from December 2002 through April 2004.

LEGEND:

⊕ GW6-4	Well Location identified from a report titled "Former Air Force Plant No. 51, HTRW Investigation, Greece, NY" by Ogden Environmental And Energy Services Co., Inc, dated April 2000
AOC1	Area Of Concern with Numbered Designation
◆ MW1-1	Monitoring Well with Designation
⊕ TB-2	Test Boring with Designation
—*500*—	Total VOC Contour Line (ppb) Created By Golden Software, Inc. Surfer8 Program

DATE	01-2007
FIELD VERIFIED BY	JAD
DATE DRAWN	01-17-2007
DRAWN BY	RJM
DATE ISSUED	01-17-2007
SCALE	1" = 50'

day
DAY ENVIRONMENTAL, INC.
ENVIRONMENTAL CONSULTANTS
ROCHESTER, NEW YORK 14614-1008
NEW YORK, NEW YORK 10165-1617

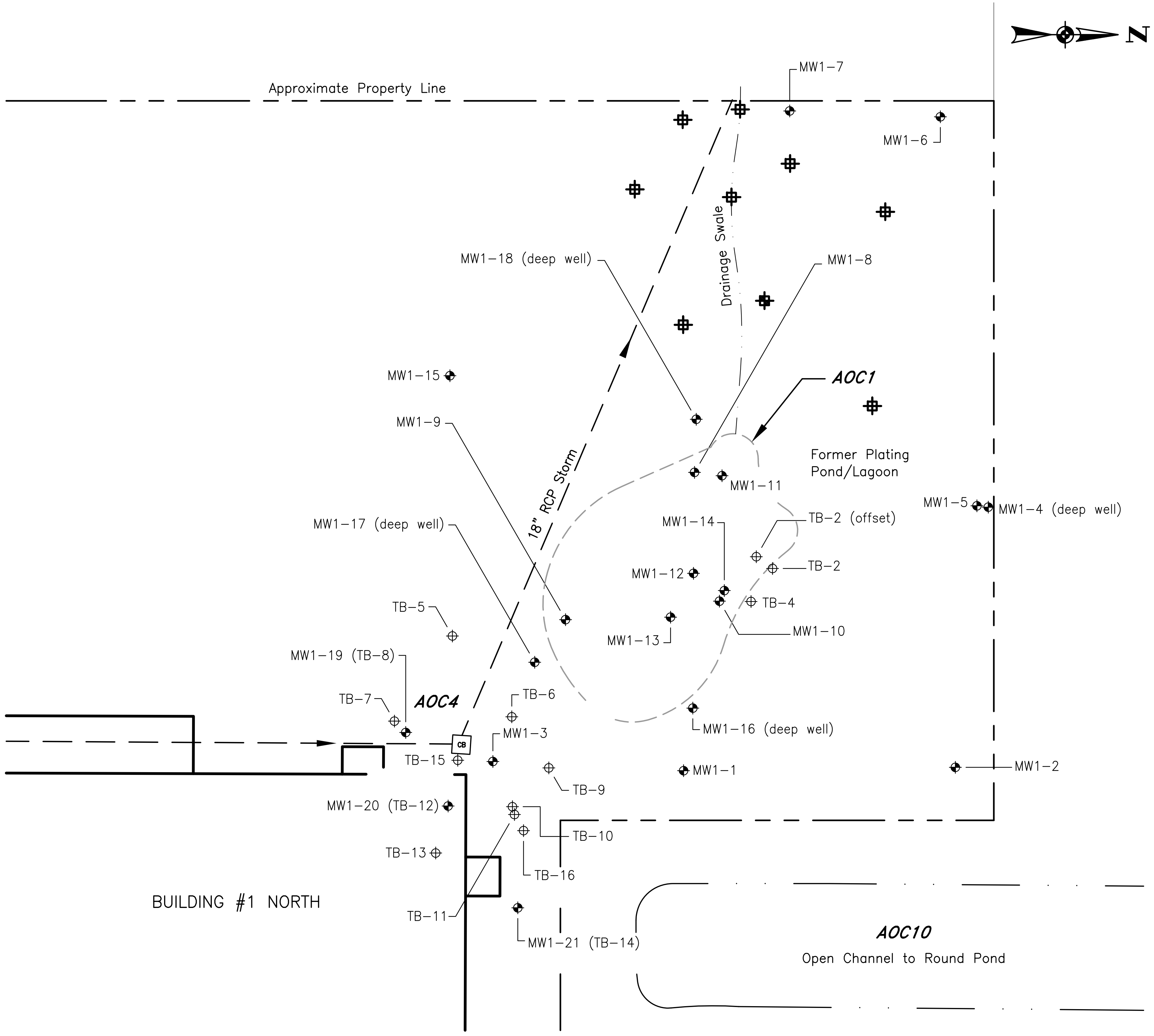
PROJECT TITLE
4777 DEWEY AVENUE
GREECE, NEW YORK

OU1 REMEDIAL WORK PLAN

DRAWING TITLE
Total VOCs in Groundwater Contour Map

PROJECT NO.
2806S-01

AOC1-I



Test Location Plan

1" = 50'

NOTES:

1. Monitoring Well MW1–1 thru MW1–10 are 2" PVC wells installed December 2002.
2. Monitoring Wells MW1–11 thru MW1–14 are 4" Stainless Steel wells installed July 2003.
3. Monitoring Well MW1–15 thru MW1–21 are 2" PVC wells installed March 2004.
4. Drawing prepared from Figure GEN–2 in the general work plan dated June 2002 and site observations by representatives of Day Environmental, Inc. from December 2002 through April 2004.

LEGEND:

AOC1	Area Of Concern with Numbered Designation
◆ MW1–1	Existing Monitoring Well with Designation
⊕ TB–2	Existing Test Boring with Designation
✥	Proposed Remedial Design Overburden Monitoring Well Location
⊕	Proposed Remedial Design Test Boring Location

DATE	01-2007
DesignTag	JAD
DATE DRAWN	01-17-2007
DRAWN BY	CPS
DATE ISSUED	01-17-2007
SCALE	AS Noted

day
DAY ENVIRONMENTAL, INC.
ENVIRONMENTAL CONSULTANTS
ROCHESTER, NEW YORK 14614-1008
NEW YORK, NEW YORK 10165-1617

PROJECT TITLE
4777 DEWEY AVENUE
GREECE, NEW YORK

OU1 REMEDIAL WORK PLAN

DRAWING TITLE
Proposed Remedial Design Test Locations

PROJECT NO.
2806S-01

AOC1-J

Ref1:
Ref2:
Ref3:

Ref4:
Ref5:
Ref6:

Xerox432AnsiB-2; 11 x 17
Layout Name: OU1 RWP

Time Plotted: Wed Jan 17 14:35 2007
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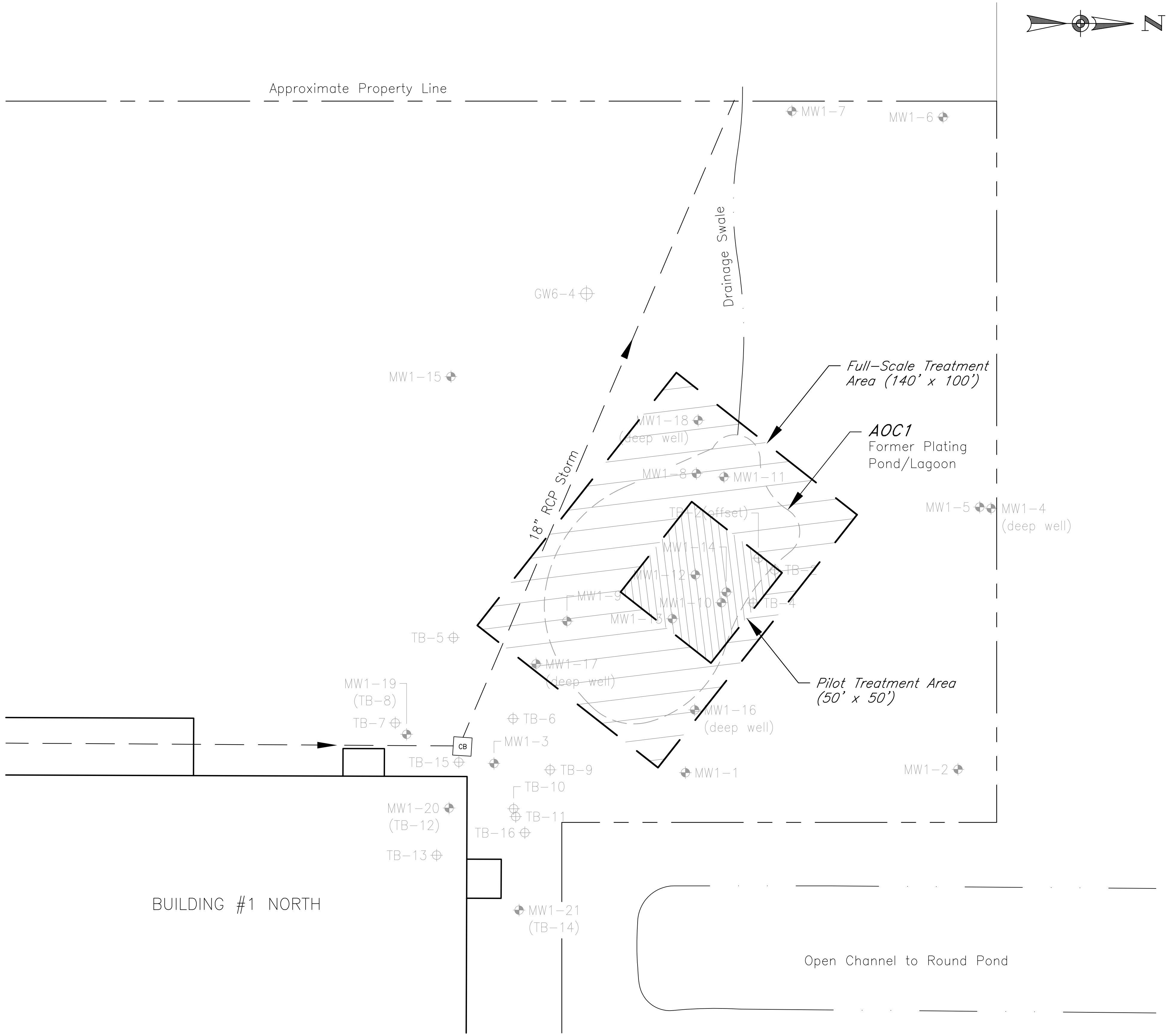


Test Location Plan
1" = 50'

NOTES:

1. Monitoring Well MW1-1 thru MW1-10 are 2" PVC wells installed December 2002.
2. Monitoring Wells MW1-11 thru MW1-14 are 4" Stainless Steel wells installed July 2003.
3. Monitoring Well MW1-15 thru MW1-21 are 2" PVC wells installed March 2004.
4. Drawing prepared from Figure GEN-2 in the general work plan dated June 2002 and site observations by representatives of Day Environmental, Inc. from December 2002 through April 2004.

LEGEND:

⌖ GW6-4	Well Location identified from a report titled "Former Air Force Plant No. 51, HTRW Investigation, Greece, NY" by Ogden Environmental And Energy Services Co., Inc, dated April 2000
AOC1	Area Of Concern with Numbered Designation
◐ MW1-1	Monitoring Well with Designation
⌖ TB-2	Test Boring with Designation

FIELD VERIFIED BY **JAD**	DRAWN BY **RJM**	SCALE **1" = 50'**
DATE **01-2007**	DATE DRAWN **01-17-2007**	DATE ISSUED **01-17-2007**

DAY ENVIRONMENTAL, INC.
ENVIRONMENTAL CONSULTANTS
ROCHESTER, NEW YORK 14614-1008
NEW YORK, NEW YORK 10165-1617

PROJECT TITLE
4777 DEWEY AVENUE
GREECE, NEW YORK

OU1 REMEDIAL WORK PLAN

DRAWING TITLE
Tentative In-Situ Chemical Oxidation Treatment Areas

PROJECT NO.
2806S-01

AOC1-K

APPENDIX A

Table 1 (Opinion of Probable Cost of Selected Remedy)

TABLE 1

Opinion of Probable Cost of Selected Remedy
Operable Unit OU1
Former Air Force Plant No. 51
4777 Dewey Avenue
Greece, New York

Design-Phase Investigation, In-Situ Chemical Oxidation of Source Area, Post-Treatment Groundwater Monitoring, and Institutional Controls

Capital/Initial Costs	
Design-Phase Investigation	$20,000
In-Situ Chemical Oxidation of Source Area	
Pilot Phase	$191,000
Full-Scale Phase	$400,000
Polishing Phase	$96,000
Institutional Controls	$35,000
20% Contingency	$148,400
Total	**$890,400**
Operation/Maintenance Annual Costs	
Year 1 Groundwater Monitoring ($30,000 X 1 yr)	$30,000
Years 2-5 Groundwater Monitoring ($15,000 X 4 yrs)	$60,000
Remediation-Derived Waste ($7,000 X 2 Yrs)	$14,000
Remediation-Derived Waste ($2,000 X 3 Yrs)	$6,000
20% Contingency	$22,000
Total Operation/Maintenance Annual Costs	**$132,000**
Closeout Costs	
Reports	$35,000
20% Contingency	$7,000
Total Closeout Costs	**$42,000**
Present Worth Cost	
Capital/Initial Costs*	$890,400
Year 1 Groundwater Monitoring Present Worth (F=0.952)*	$34,272
Years 2-5 Groundwater Monitoring Present Worth (F=4.3295-0.952)*	$60,786
Years 1-2 Remediation-Derived Waste Present Worth (F=1.8594)*	$15,616
Years 3-5 Groundwater Monitoring Present Worth (F=4.3295-1.8594)*	$5,928
Closeout Costs (F= 0.9070)*	$38,094
Total Present Worth Cost	**$1,045,096**

F = Discount Factor of 5% at the nth year of the project

* = Includes 20% contingency

APPENDIX B

Geo-Cleanse International, Inc.
Statement of Qualifications

Geo-Cleanse®
INTERNATIONAL, INC.

August 31, 2006

Mr. Jeffrey A. Danzinger
Day Environmental, Inc.
40 Commercial Street
Rochester, New York 14614-1008

Re: Statement of Qualifications (SOQ)

Dear Mr. Danzinger:

Geo-Cleanse International, Inc. (GCI) is pleased to present the following statement of qualifications introducing the patented Geo-Cleanse® remedial technology. GCI appreciates your interest and should you have any questions, please do not hesitate to contact MariKay Fish or myself at (908) 206-1250 or via e-mail mfish@geocleanse.com.

Thank you for considering Geo-Cleanse® International to assist you in your remedial needs.

Sincerely,

William Moody
Assistant Project Manager
Geo-Cleanse International, Inc.

Geo-Cleanse International, Inc.

Statement of Qualifications
for
Day Environmental, Inc.

40 Commercial Street
Rochester, NY 14614-1008

August 30, 2006

NOTICE

This document and its contents are the property of Geo-Cleanse International. Inc. It is delivered in the expressed condition that it is not to be disclosed. reproduced in whole or part, or used for any other purpose other than in connection with the Geo-Cleanse® Process as applied by Geo-Cleanse International, Inc., for the referenced site. No right is granted to the recipient to disclose or use any information contained in this document. United States patents protect the Geo-Cleanse® Process and only Geo-Cleanse International, Inc. may apply the Geo-Cleanse® Process.

Geo-Cleanse International, Inc
4 Mark Road, Suite C
Kenilworth, NJ 07033
Tel (908) 206-1250
Fax (908) 206-1251

www.geocleanse.com

TABLE OF CONTENTS

Description **Page**

1.0 Introduction

2.0 General Information

3.0 Technical Information

4.0 Performance

5.0 Personnel

6.0 Safety

7.0 Chemical Oxidation Applicability

FIGURES

1.0 INTRODUCTION

1.1 Introduction

Geo-Cleanse International, Inc. (GCI) is an environmental remediation company dedicated to in-situ chemical oxidation of organic contaminants in both soil and groundwater. The contact information of GCI is as follows:

Address:	Geo-Cleanse International, Inc. 4 Mark Road, Suite C Kenilworth, NJ 07033
Phone:	(908) 206-1250
Fax:	(908) 206-1251
E-Mail:	mfish@geocleanse.com
Internet Address:	www.geocleanse.com
Main Contact:	MariKay Fish

GCI was incorporated in 1995 to commercially apply the Geo-Cleanse® Process. United States Patents 5,525,008 and 5,611,642, which cover the delivery methodology and the injection equipment, were issued to GCI. GCI possesses the commercial rights to these patents.

Chemical oxidation of organic contaminants is achieved by injection of hydrogen peroxide and a catalyst formulation or sodium permanganate into the affected media under carefully controlled conditions. The Geo-Cleanse® Process is a technology designed to simultaneously inject hydrogen peroxide and trace quantities of metallic salts or sodium permanganate under pressure into the impacted media via a patented methodology and equipment. This in-situ chemical oxidation system is capable of complete, non-selective oxidation of organic compounds in soil and groundwater. The basic reaction in the Geo-Cleanse® Process is simplified below:

Chemical Oxidant + Organic Contaminant → Carbon Dioxide + Water + Chloride ions
(Chloride ions are only expected on chlorinated sites)

To date, GCI has full-scale field experience on over 100 sites in twenty-five states, Canada, and Europe. GCI has experience remediating a wide variety of contaminants including petroleum, pesticide, coal tars, and chlorinated hydrocarbons. A proven strength of the Geo-Cleanse® Process is the ability to remove free phase DNAPL.

Our past and current experience with DOE and DOD projects in addition to our other private industry projects illustrates GCI's success, ability, resources, and experience to perform on both small private industry sites and larger scale government sites.

2.0 GENERAL INFORMATION

2.1 The Geo-Cleanse Process and Fenton's Chemistry

The Geo-Cleanse® Process is a patented technology to simultaneously inject hydrogen peroxide and trace quantities of iron salts under pressure to the subsurface in order to destroy organic contaminants in soil and groundwater. U.S. patents 5,525,008 and 5,611,642 protect the injection technology. The Geo-Cleanse® Process delivers a calculated charge of hydrogen peroxide and catalyst to the contaminated region via specially designed injection equipment consisting of mixing heads and subsurface injectors. The patented injection methodology and equipment are the keys to the Geo-Cleanse® Process.

The chemistry involved is based upon Fenton's reagent. In 1894, H.J.H. Fenton reported that malic acid was rapidly oxidized by hydrogen peroxide in the presence of iron salts. Haber and Weiss (1934) identified the oxidation mechanism resulting from mixtures of hydrogen peroxide and ferrous iron (referred to as Fenton's reagent) as a hydroxyl free radical ($OH\cdot$) formed by the reaction:

$$H_2O_2 + Fe^{+2} \rightarrow Fe^{+3} + OH\cdot + OH^- \qquad (1)$$

where H_2O_2 is hydrogen peroxide, Fe^{+2} is ferrous iron, Fe^{+3} is ferric iron, $OH\cdot$ is hydroxyl free radical, and OH^- is hydroxyl ion. Fenton's reagent chemistry is complex, involving a number of additional reactions producing both oxidants and reductants that contribute to contaminant destruction (e.g., Watts et al., 1999):

$$OH\cdot + Fe^{+2} \rightarrow OH^- + Fe^{+3} \qquad (2)$$

$$Fe^{+3} + H_2O_2 \rightarrow H^+ + HO_2\cdot + Fe^{+2} \qquad (3)$$

$$Fe^{+2} + HO_2\cdot \rightarrow Fe^{+3} + HO_2^- \qquad (4)$$

$$Fe^{+3} + HO_2\cdot \rightarrow Fe^{+2} + O_2 + H^+ \qquad (5)$$

$$OH\cdot + H_2O_2 \rightarrow H_2O + HO_2\cdot \qquad (6)$$

where $HO_2\cdot$ is hydroperoxyl radical, HO_2^- is hydroperoxyl anion, O_2 is molecular oxygen, H^+ is hydronium ion, and H_2O is water. Additional reactions occur with organic compounds. The suite of reactions associated with Fenton's reagent is complex, but very effective at destroying many organic compounds dissolved in groundwater, sorbed to soil particles, or existing as non-aqueous phase liquids in subsurface environments. Fenton's reagent is generally most efficient under acidic pH conditions (pH 4-6) because oxidation of iron from the ferrous to ferric state by reactions other than that in equation 1 is minimized, ferric iron hydrous oxyhydroxides are less likely to precipitate (removing iron from solution), and bicarbonate (which competes with the organic compounds for the hydroxyl radical) is absent. An effective (although not chemically optimal) Fenton's reagent system can be established at a pH greater than 6.

The hydroxyl free radical generated by Fenton's reagent is a powerful, non-selective oxidant. Oxidation of an organic compound by Fenton's reagent is a rapid and exothermic (heat-producing) reaction. Rate constants for reactions of hydroxyl free radicals with common environmental pollutants are typically in the range of 10^7 to 10^{10} $M^{-1}s^{-1}$ (e.g., Buxton et al., 1988; Haag and Yao, 1992), and 100% mineralization is generally complete in minutes. Intermediate compounds are primarily naturally occurring carboxylic acids. The end products of oxidation are primarily carbon dioxide and water, plus chloride (in the case of chlorinated compounds) and nitrate (in the case of nitroaromatic compounds). None of the injected reagents pose an environmental hazard. Unconsumed hydrogen peroxide naturally degrades to oxygen and water, typically within a few days of injection.

Site characterization data provided by Day Environmental, Inc. indicates that the primary organic contaminants present at the site are chlorinated solvents, primarily TCE. Fenton's reagent oxidizes chlorinated aliphatic compounds such as TCE and its natural degradation products to substituent carbon dioxide, water, and chloride, via an oxidation pathway that involves carboxylic acids. The oxidation pathway is not a dehalogenation process like natural biodegradation, and additional cis-1,2-DCE and vinyl chloride (VC) are not produced by Fenton's reagent oxidation. Reported rate constants for reaction of $OH^{\cdot}$ with TCE range from 4.0 - 4.3 x 10^9 $M^{-1}s^{-1}$ (Buxton et al., 1988), indicating an extremely rapid reaction. Oxidation of TCE ($Cl_2C{=}CHCl$) by Fenton's reagent produces dichloroacetic acid ($CHCl_2COOH$) as the only significant intermediate product, which is further oxidized to formic acid ($HCOOH$) and finally to water (H_2O), carbon dioxide (CO_2), and chloride (Cl^-) (**Figure 1**):

$$Cl_2C{=}CHCl + OH^{\cdot} + H_2O \rightarrow CHCl_2COOH + 2H^+ + Cl^-$$
$$CHCl_2COOH + 2OH^{\cdot} \rightarrow HCOOH + 2H^+ + 2Cl^- + CO_2$$
$$HCOOH + 2OH^{\cdot} \rightarrow 2H_2O + CO_2$$

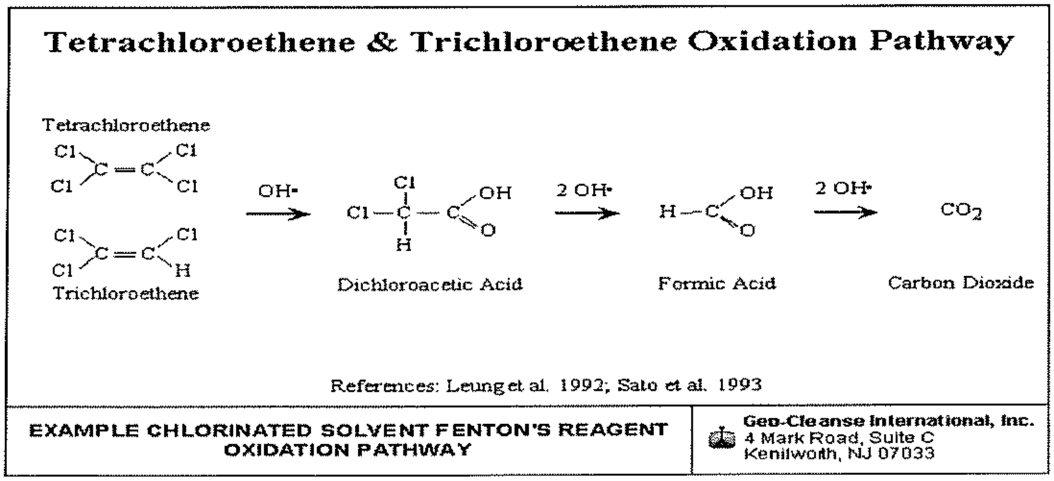


Figure 1: Oxidation Pathway of PCE and TCE

Fenton's reagent effectively and completely oxidizes TCE and its related compounds to stoichiometric quantities of carbon dioxide, water, and chloride in soil and groundwater under laboratory-simulated conditions (e.g., Ravikumar and Gurol, 1994; Gates and

Siegrist, 1995) and in GCI field experience (e.g., Bryant and Wilson, 1998, 1999; Levin et al., 2000; Maughon et al., 2000).

The Geo-Cleanse® Process delivers a calculated charge of hydrogen peroxide and catalyst to the contaminated region via a patented injection methodology and equipment. The methodology and equipment are the keys to the Geo-Cleanse® Process. Each injector contains a mixing head that promotes mixing of reagents and stimulates circulation of groundwater. This promotes rapid reagent diffusion and dispersion through the impacted zone. All reagents are injected into the subsurface through the injectors. When acceptable conditions are established, peroxide and catalyst will be injected simultaneously. The mixing heads ensure that catalyst and peroxide will not combine and react within the sealed system until they reach the screened interval of the injector. The injected reagents are kept separate via a constant pressure delivery system complete with check valves that prevents the mixing of chemicals before they reach the treatment zone. **Figure 2** shows the expected pattern of the injected reagents.

The patented injectors are also specially designed to withstand the elevated temperatures and pressures resulting from a Fenton's reagent reaction within the zone of contamination.

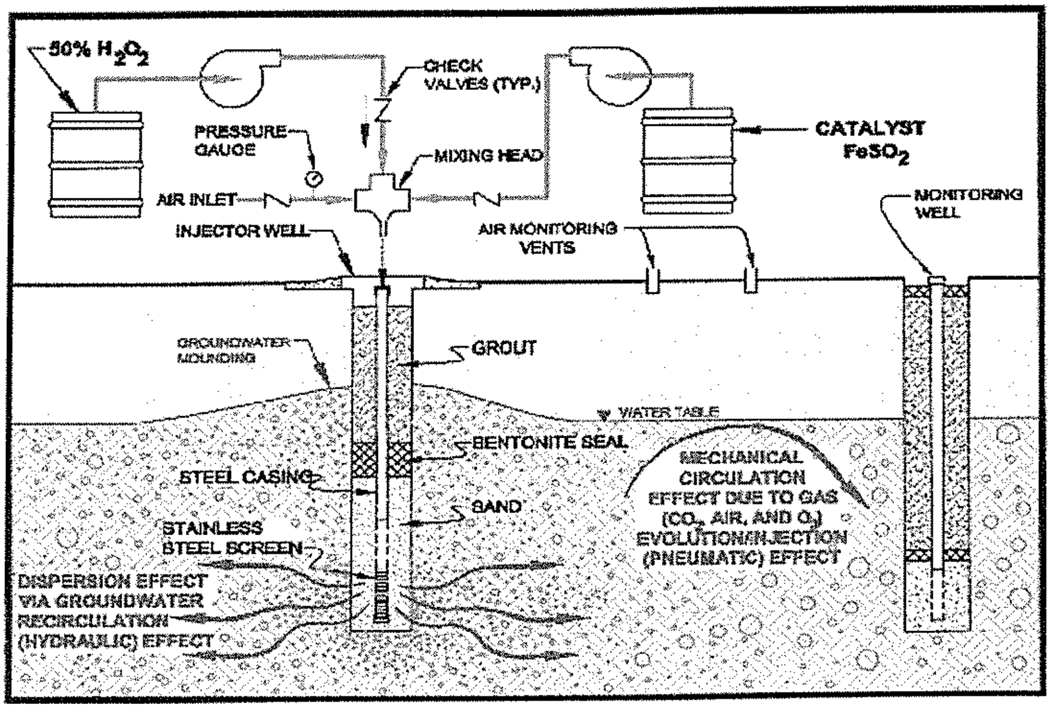


Figure 2: Expected Pattern of Injected Reagents

2.2 Underlying Principal

The general underlying scientific principal of the Geo-Cleanse® Process is to take a proven chemical reaction from the wastewater industry and apply it to the subsurface. In the initial design of the process, GCI determined that there were three design goals that would need to be achieved. These goals were:

1) Create the free radical in the formation in contact with the contaminant.
2) Establish an effective radius of influence from each injector.
3) Deliver the reagents to the sub-surface in a quick, safe, and economical way.

With these goals in mind, GCI determined the delivery system was the key to the effectiveness of in-situ chemical oxidation. GCI's pressurized delivery system is fundamental to the Geo-Cleanse® Process. The GCI delivery system creates the greatest probability that the hydroxyl free radical will form in contact with the contaminants, enabling their destruction.

2.3 Distinguishing Characteristics

The Geo-Cleanse® Process, which is proprietary to Geo-Cleanse International, Inc. (GCI) is a technology to inject hydrogen peroxide and trace quantities of metallic salts and permanganate into the impacted media via a patented methodology and equipment (US Patents 5,525,008 and 5,611,642). The main difference between GCI and other companies using hydrogen peroxide and permanganate is that our system is pressurized and does not depend on diffusion of the reagents into the groundwater. Instead, GCI depends on a pressure gradient and secondary permeability to move the reagents through the formation.

3.0 TECHNICAL INFORMATION

3.1 Injector Information

The Geo-Cleanse® Process utilizes patented and specialized injector points on all of our project sites. The final project design determines the screen lengths and the quantities of the building materials. The components of typical injectors are as follows:

- ¾" - 1 ¼" diameter x 3-6 ' long, CPVC drive points with 60 gauze (.010-slot) screen
- ¾" – 1 ¼" couplings, Schedule 80 CPVC
- ¾" – 1 ¼" riser pipe, Schedule 80 CPVC
- ¾" – 1 ¼" threaded caps, Schedule 80 CPVC
- Specialized grout ratio
  (94 lbs Type 1 Portland Cement: 2.8 lbs bentonite powder: 7.4 gal water).

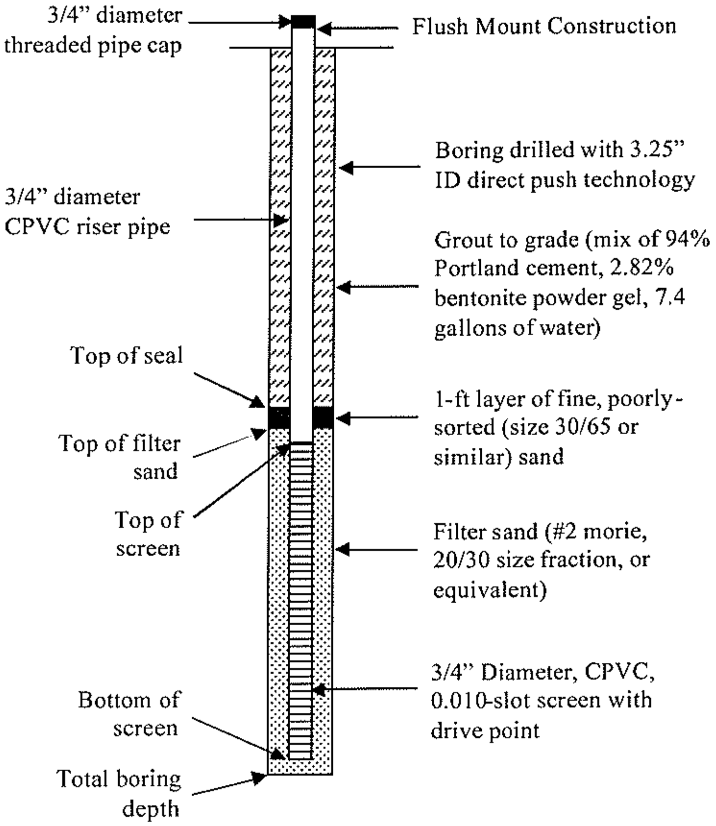


Figure 3: Cross Section of a Typical Geo-Cleanse® Injector

A pipe cutter and a threader are necessary for the installation of the injectors and vent wells.

3.2 Injection Equipment

The Geo-Cleanse® Process utilizes a specialized mobile treatment vehicle and patented injection heads to deliver to the subsurface.

This injection vehicle is specifically designed to control delivery of the reagents used in the Geo-Cleanse® Process. Safety and efficiency were the design goals for the injection vehicle. A picture of a typical injection vehicle is included below in **Figure 4**:

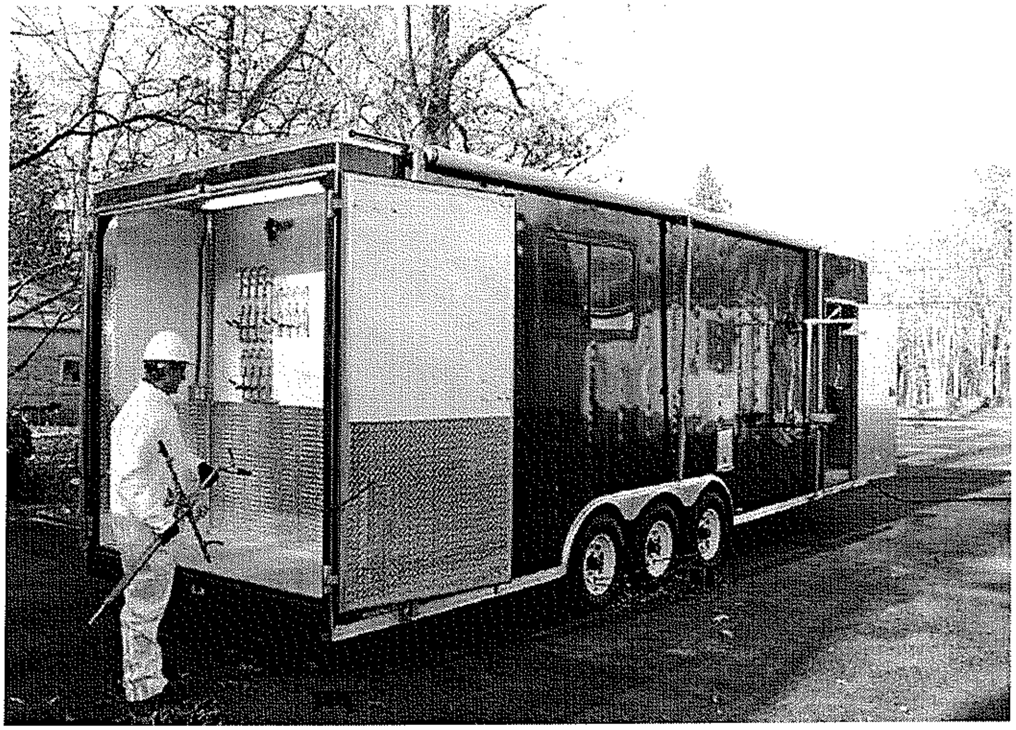


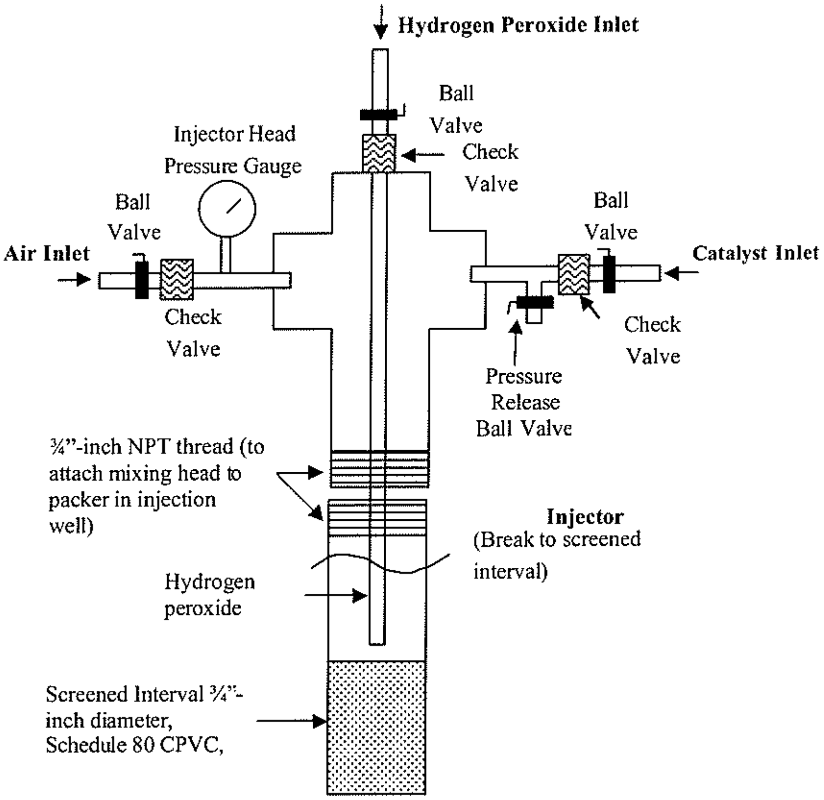
Figure 4: View of Injection Vehicle

The view of the injection vehicle shows the control board, which allows the operator to independently control the flow of reagents and injection pressures to each of the four mixing heads.

The injector mixing heads are specifically designed to control and mix the reagents used during the Geo-Cleanse® Process. **Figure 5** shows the general design of an injection head.

The injector head has a duplicate set of ball valves to control the flow of catalyst, hydrogen peroxide, and air as a secondary and backup control. The injectors are constructed of stainless steel and have a pressure relief valve at the base for added safety.

The ability to monitor the flow of reagents is present at control board of the injection vehicle, the control valves of the injector heads, and the control valves of the reagent storage tanks. This redundant control is established for health and safety reasons.



U.S. Patents 5,525,008 and 5,611,642

Figure 5: Patented Geo-Cleanse® Injector Head Cross Section

3.3 Chemicals Utilized

Hydrogen Peroxide (50% Tech Grade)
Injected into the impacted soils and groundwater at concentrations = 25% with resultant concentrations to groundwater of less than 1%. This concentration quickly falls to less than 25 ppm within several hours following the injection and will be completely gone in 2-3 days.

Purpose: Oxidizing agent

Ferrous Sulfate (Iron Sulfate Heptahydrate)
Injected into the soils and groundwater at a 100 ppm concentration in a catalyst blend which typically results in concentrations in groundwater of less than 10 ppm. This concentration will be precipitated as a ferric oxide or hydroxide and therefore removed from solution.

Purpose: Catalyst

*** Sulfuric Acid (66° or 98%)**
Several ounces are added to 275 gallons of water-based catalyst blend (to establish a pH of ~4) which is injected into the soils and groundwater. This acidic water is used to adjust the pH of the water.

Purpose: pH adjustment

*** Phosphoric Acid (85% Tech Grade)**
Several ounces are added to 275 gallons of water-based catalyst blend (to establish a pH of ~4) which is injected into the soils and groundwater. This acidic water is used to adjust the pH of the water.

Purpose: pH adjustment

*** Calcium Phosphate**
Two ounces are added to 275 gallons of water based catalyst blend which is injected into the soils and groundwater. This agent helps stabilize the reaction.

Purpose: Stabilization

*** may or may not be added depending on site specific conditions.**

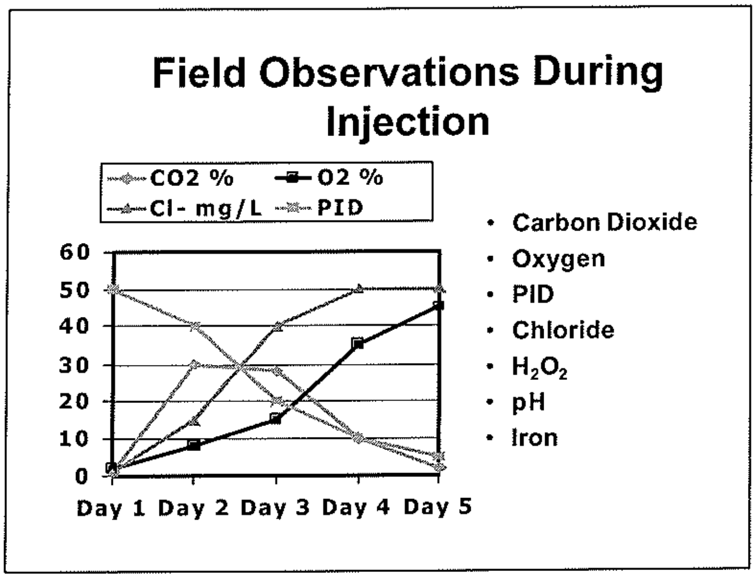
3.4 Fate of the Injected Chemicals

Following a GCI ISCO treatment, none of the injected chemicals are recovered. Hydrogen peroxide will break down into oxygen and water within days of our injection, the ferrous ion is precipitated as a ferric oxide or hydroxide, therefore removed from solution and buffering materials within the aquifer neutralize the acids. The pH shift returns to normal background conditions after the injection.

3.5 Sampling Parameters Utilized While Injecting

For Fenton's chemistry injection, GCI routinely monitors pH, dissolved iron, hydrogen peroxide, chloride (if a chlorinated contaminated site), and headspace analysis in groundwater. We also monitor the carbon dioxide and oxygen in the off gas produced by the chemical oxidation.

During a typical Fenton's Chemistry application, one would expect to see the CO_2 production to follow a bell shaped curve. At the beginning of the injection, the CO_2 levels will begin to rise as the carbon of the contaminant is destroyed. As the injection progresses, the carbon dioxide levels begin to stabilize. Since carbon dioxide is an end product of the reaction between the hydroxyl free radical and the contaminant, this indicates that there is no longer contaminant present within this region. At the same time, the oxygen will continuously climb as the carbon from the contaminant is not available and the free radicals consume themselves. The chlorides will also experience a steady climb as the oxidation breaks down the chlorinated compound. Typical observations are plotted on **Figure 6**.



Field Observations During Injection

- Carbon Dioxide
- Oxygen
- PID
- Chloride
- H_2O_2
- pH
- Iron

Figure 6: Typical Field Observations

4.0 Performance

4.1 Project Experience with Chlorinated Contaminated Sites

Pilot Testing and Full-Scale Applications

1) *Anniston Army Depot-* In July 1997, the first large-scale use of the patented Geo-Cleanse® Process for removal of dense non-aqueous phase liquid (DNAPL) chlorinated solvents and hydrocarbons began over an area of approximately 2 acres at a former clay backfilled lagoon site on Anniston Army Depot (ANAD), Anniston, Alabama.

   This rapid *in-situ* technology was used to reduce volatile organic compounds to approved risk-based cleanup levels on over 43,125 cubic yards (yd^3) of soils containing up to 31-percent trichloroethene, methylene chloride, daughter products, and BTEX. Soil injection extends from 6 feet (ft) to at least 25 ft below grade. Groundwater pockets of high strength DNAPL in residual sludge layers and associated clay smear zone are being eliminated selectively from 29 to 71 ft (top of bedrock) to prevent overlying soil recontamination.

   The full-scale 155-day injection of up to 132,925 gallons (gal) of peroxide into 255 injectors was completed in March 1999 and a polish was completed in May 2000. Soil concentrations of up to 21,760,000 micrograms per kilogram (mg/kg) were reduced to below detection.

2) *Kings Bay Naval Submarine Base, Georgia:* The Geo-Cleanse® Process was used to remediate a contaminated source area of 48,000 cubic feet. The area was contaminated with PCE, TCE, DCE, and VC. The initial total chlorinated aliphatic compounds were detected at concentrations of more than 9,000 ppb in groundwater. PCE concentrations were as much as 5% of the pure solubility phase, indicating the presence of DNAPL.

   A total of 44 injectors were installed and approximately 23,292 gallons of Fenton's reagent, which includes hydrogen peroxide and ferrous iron catalyst, were injected during a multi phased injection program. GCI was able to reduce the contaminant concentrations to below the cleanup goal of 100 ppb.

3) *Pensacola Naval Air Station, Florida:* The Geo-Cleanse® Process was utilized to remediate 3,000 cubic yards of soil and 16,400 gallons of groundwater at this site. Initial concentrations of TCE were approximately 1,534 ppb.

   GCI utilized 15 injectors and injected approximately 10,127 gallons of hydrogen peroxide during a multi phased remediation. GCI effectively reduced the TCE concentrations to 37 ppb.

4) *Letterkenny Army Depot, Pennsylvania:* The Geo-Cleanse® Process was used at this site to treat 2,692,800 gallons of contaminated groundwater. This groundwater plume was located within a limestone bedrock aquifer at this site. The contaminants

of concern were PCE, TCE, and DCE and their initial concentrations were 218 ppb, 2,138 ppb and 860 ppb respectively.

GCI utilized 6 open hole injectors and 12,635 gallons of hydrogen peroxide to remediate this site. GCI was able to reduce contaminant concentrations to 130 ppb PCE, 1,282, ppb TCE, and 516 ppb of DCE.

5) *Westinghouse Savannah River Company, South Carolina:* An in-situ chemical oxidation of DNAPL using Fenton's Reagent was performed at this site. The site was a 50' x 50' area located in the DNAPL source area. The treatment zone consisted of a 64,000 cubic foot volume of soil containing approximately 600 pounds of DNAPL. Average contaminant concentrations in the treatment area groundwater were 119.49 ppm of PCE and 21.31 ppm of TCE.

   GCI installed four injectors and four monitoring wells in the treatment area and achieved a 94% reduction. The average PCE concentration was reduced to 0.65 ppm and the average TCE concentration was reduced to 0.07 ppm.

6) *Confidential Dry-Cleaning Facility, Washington:* GCI was contracted to perform an in-situ chemical oxidation (ISCO) at this site. The treatment area was approximately 20' x 80'. The contamination extended to a depth of 6' to 13' below grade. The average initial contaminant concentrations were 8,500 ppb of PCE, 550 ppb of TCE, and 24 ppb of cis-DCE, for a total CVOC concentration of 9,074. The initial concentrations of PCE exceed the 1% water solubility rule and indicate the presence of DNAPL.

   GCI installed thirteen injection points and injected approximately 8,257 gallons of hydrogen peroxide over the duration of the treatment. The post-treatment average total CVOC concentration was reduced to 90 ppb.

7) *Naval Air Station South Weymouth, Massachusetts:* GCI was contracted to perform an ISCO treatment using Fenton's Reagent at the above referenced site. The impacted area was located within a bedrock aquifer. Pre- injection concentrations of PCE were approximately 980 ppb.

   GCI installed 51 bedrock injectors and injected 12,596 gallons of hydrogen peroxide during the course of the treatment. Post- injection contaminant concentrations were reduced to a range of ND to 200 ppb of PCE.

8) *Confidential Industrial Client, New Jersey:* GCI was contracted to perform an in-situ chemical oxidation treatment at this site. The treatment area was approximately 1 acre in area and approximately 40 ft thick, spanning from 5 ft bgs to 45 ft bgs. The treatment area contained contaminants such as PCE, TCE, Cis-DCE, Trans-DCE, and VC. The total VOC concentration was reduced by greater than 95% at this site.

4.2 Past Performance / References

GCI has completed over 100 projects involving the government and private industry. GCI has treated a numerous types of contaminants in varied lithologies. GCI is the only full-service chemical oxidation treatment company with the ability to mobilize up to 10 treatment vehicles to a site to meet our client's scheduling needs.

4.3 States of Operation

The following is a list of states in which GCI has operated: Alabama, California, Colorado, Connecticut, Florida, Georgia, Illinois, Kansas, Massachusetts, Michigan, Minnesota, Missouri, Nebraska, Nevada, New Hampshire, New Jersey, New York, North Carolina, Ohio, Pennsylvania, South Carolina, Tennessee, Texas, Washington, Wisconsin & Canada.

5.0 Personnel

5.1 Profiles

Geo-Cleanse International, Inc (GCI) is committed to providing the highest level of service and performance. This requires a philosophy directed at recruiting and retaining the most competent people in their respective fields. The GCI management team is a multi-disciplined group of professionals dedicated to in situ remedial services.

6.0 Safety

6.1 Health & Safety Plan

The injection program will be conducted in accordance with applicable OSHA safety standards and according to a site specific Health and Safety Plan prepared by GCI. All personnel involved in the injection program have the required OSHA training. All injection equipment is designed and maintained with the highest level of safety in mind. GCI is proud of its spotless safety record.

Listed below is the table of contents section from a typical GCI Health & Safety plan:

1.0 Introduction
2.0 Description of Site Specific Hazards
2.1 Chemicals/Contaminants
2.2 Heavy Equipment
    2.3 Weather Related Hazards
    2.4 Chemical Transfer Hazards
3.0 Monitoring Equipment and Instruments
4.0 Training
5.0 Personnel Monitoring
5.1.1 Medical Surveillance
    5.2 Personnel Protective Equipment Monitoring
    5.3 Routine Monitoring
    5.4 Stress Monitoring
6.0 Respiratory Protection Program
    6.1 Administration
    6.2 Respirator Selection
    6.3 Respirator Type
    6.4 Training
7.0 Levels of Protection
    7.1 Level C
    7.2 Level D
8.0 Procedures for Determining Personnel Protection Level
9.0 Emergency and First Aid Equipment and Communications
10.0 Emergency Procedures
11.0 On Site Evacuation Plan
12.0 Personal Injury
13.0 Decontamination Procedures
    13.1 Personal Decontamination
    13.2 Heavy Equipment and Vehicle Decontamination
    13.3 Waste Disposal

6.2 Safe Handling of Chemicals

The mixing heads ensure that catalyst and peroxide will not mix together in the sealed system until they are at the screened interval of the injector.

For a more descriptive overview of how the chemicals are stored, handled and injected see section **3.2 Injection Equipment.**

6.3 Safety Devices

The entire system has redundant safety and control devices. The flow of reagents can be controlled at three places: 1) the control board, 2) the injector head, and 3) the pumps.

The entire system has redundant check valves at the control board and at the injectors.

Each injector also has a rupture disk set a 250 psi that if tripped will vent from approximately six inches above the ground into the well vault.

6.4 Personal Protection Equipment

For a typical site, all workers within the exclusion zone are dressed in a modified level D consisting of: Tyvek body suit, nitrile gloves, rubber boots, OSHA approved safety glasses and hardhat when required. Other levels of protection can be utilized if circumstances warrant. **Figure 7** shows a typical GCI injection specialist.

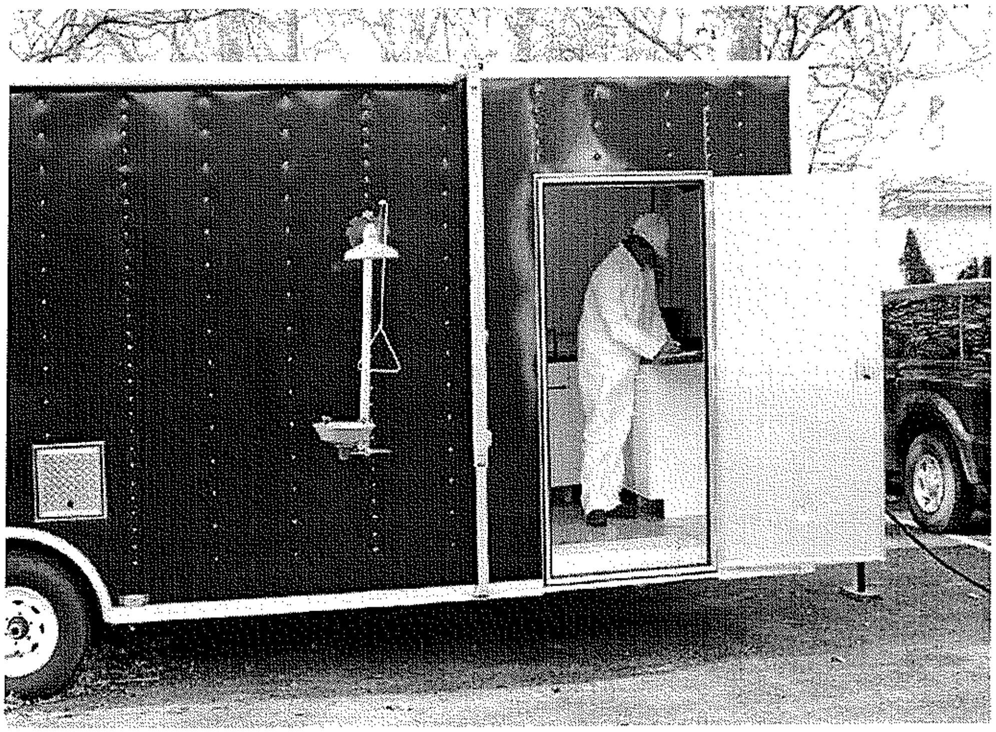


Figure 7: GCI Field Injection Specialist and Safety Shower

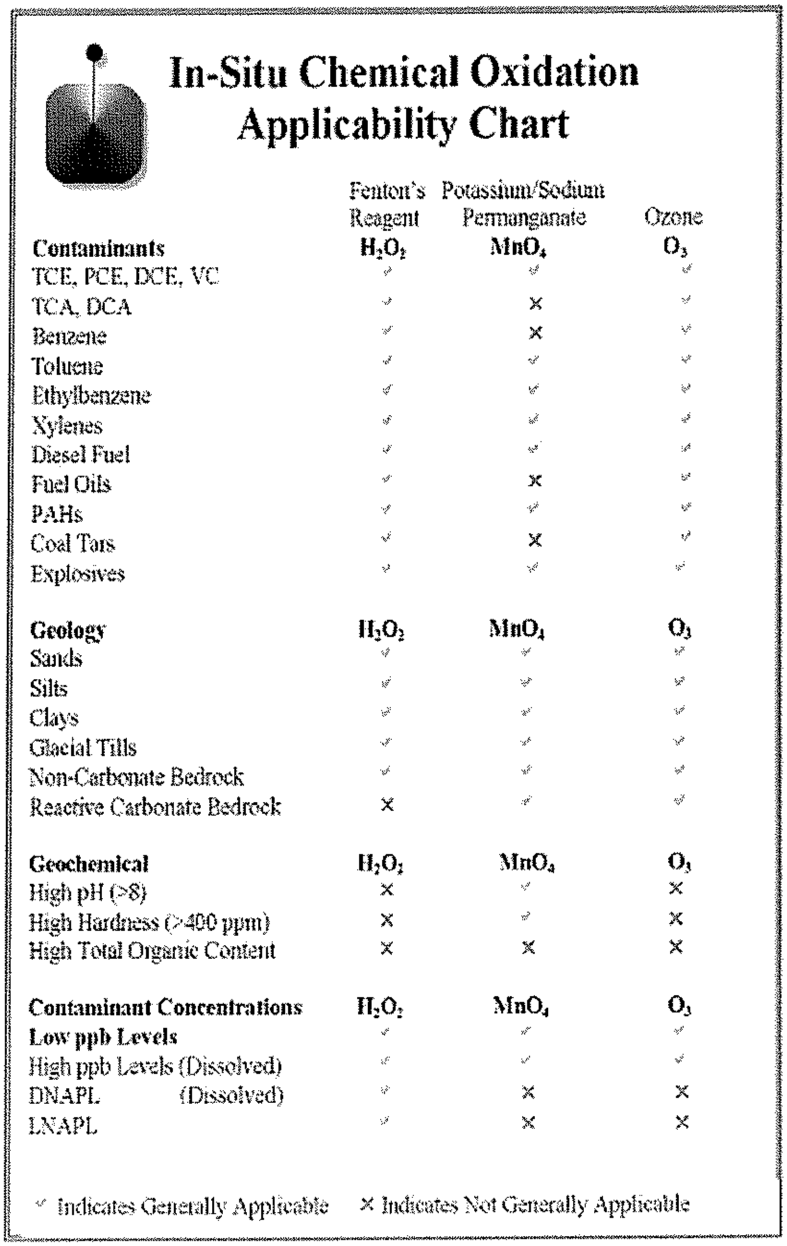
Water is available throughout the site. Water is the best way to handle exposure to permanganate and hydrogen peroxide. All vehicles have a hose in the mixing area and an eyewash station in the control area. The area where the injectors are also has a hose. There is also a full body shower / eyewash station brought to each site.

Continuous monitoring of the breathing zone ensures the quality of the air in the exclusion zone. GCI has never had to operate with any breathing apparatus but as the Health and Safety Plan shows we are prepared to do so if levels exceed standard safety levels.

7.0 Chemical Oxidation Applicability

7.1 The application of in-situ chemical oxidation

In-situ chemical oxidation can be performed using a variety of oxidants to remediate different types of contaminants in varying environments. Using our vast experience, GCI has formed a general applicability chart that indicates the oxidants that should be used to remediate certain contaminants and which oxidants can be applied most effectively in which environments.



In-Situ Chemical Oxidation Applicability Chart

	Fenton's Reagent	Potassium/Sodium Permanganate	Ozone
Contaminants	**H_2O_2**	**MnO_4**	**O_3**
TCE, PCE, DCE, VC	✓	✓	✓
TCA, DCA	✓	×	✓
Benzene	✓	×	✓
Toluene	✓	✓	✓
Ethylbenzene	✓	✓	✓
Xylenes	✓	✓	✓
Diesel Fuel	✓	✓	✓
Fuel Oils	✓	×	✓
PAHs	✓	✓	✓
Coal Tars	✓	×	✓
Explosives	✓	✓	✓
Geology	**H_2O_2**	**MnO_4**	**O_3**
Sands	✓	✓	✓
Silts	✓	✓	✓
Clays	✓	✓	✓
Glacial Tills	✓	✓	✓
Non-Carbonate Bedrock	✓	✓	✓
Reactive Carbonate Bedrock	×	✓	✓
Geochemical	**H_2O_2**	**MnO_4**	**O_3**
High pH (>8)	×	✓	×
High Hardness (>400 ppm)	×	✓	×
High Total Organic Content	×	×	×
Contaminant Concentrations	**H_2O_2**	**MnO_4**	**O_3**
Low ppb Levels	✓	✓	✓
High ppb Levels (Dissolved)	✓	✓	✓
DNAPL (Dissolved)	✓	×	×
LNAPL	✓	×	×

✓ Indicates Generally Applicable × Indicates Not Generally Applicable

Figure 9: ISCO Applicability Chart

8.0 Insurance

Geo-Cleanse International, Inc. (GCI) maintains general liability, environmental liability, workers compensation and automobile insurance. A sample Certificate of Insurance will be made available upon request. GCI can name one party as an additionally insured.

INSURANCE COVERAGE SUMMARY

Geo-Cleanse International, Inc.

Type of Insurance	Carrier	Coverage Limits
General Liability	**TIG**	**$ 2,000,000 Aggregate**
		$ 1,000,000 each occurrence
Environmental Liability	**Reliance**	**If requested for additional fee**
Workers Compensation		**Statutory**
Automobile		**$ 1,000,000**

APPENDIX C

In-Situ Chemical Oxidation
USEPA August 2006 Engineering Issue
By S.G. Huling and B.E. Pivetz

United States
Environmental Protection
Agency

Engineering Issue

In-Situ Chemical Oxidation

Scott G. Huling[1] and Bruce E. Pivetz[2]

Index

I. PURPOSE

The U.S. Environmental Protection Agency (EPA) Engineering Issue Papers are a series of technology transfer documents that summarize the latest available information on specific technical issues, including fate and transport, specific contaminants, selected treatment and site remediation technologies, and related other issues. This Engineering Issue Paper is intended to provide remedial project managers (RPMs), on-scene coordinators (OSCs), contractors, and other state, industry, or private remediation managers with information to assist in the evaluation and possible selection of appropriate in-situ chemical oxidation (ISCO) remedial alternatives.

This Engineering Issue Paper provides an up-to-date overview of ISCO remediation technology and fundamentals, and is developed based on peer-reviewed literature, EPA reports, web sources, current research, conference proceedings, and other pertinent information.

II. INTRODUCTION

II.A. Background

In-situ chemical oxidation involves the introduction of a chemical oxidant into the subsurface for the purpose of transforming groundwater or soil contaminants into less harmful chemical species. There are several different forms of oxidants that have been used for ISCO; however, the focus of this Engineering Issue Paper will be on the four most commonly used oxidants: permanganate (MnO_4^-), hydrogen peroxide (H_2O_2) and iron (Fe) (Fenton-driven, or H_2O_2-derived oxidation), persulfate ($S_2O_8^{2-}$), and ozone (O_3) (Table 1). The type and physical form of the oxidant indicates the general materials handling and injection requirements. The persistence of the oxidant in the subsurface is important since this affects the contact time for advective and diffusive transport and ultimately the delivery of oxidant to targeted zones in the subsurface. For example, permanganate persists for long periods of time, and diffusion into low-permeability materials and greater transport distances through porous media are possible. H_2O_2 has been reported to persist in soil and aquifer material for minutes to hours, and the diffusive and advective transport distances will be relatively limited. Radical intermediates formed using some oxidants (H_2O_2, $S_2O_8^{2-}$, O_3) that are largely responsible for various contaminant transformations react very quickly and persist for very short periods of time (<1 sec).

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[1] U.S. EPA/ORD/NRMRL/GWERD, P.O. Box 1198, Ada, OK 74820

[2] Dynamac Corporation, 3601 Oakridge Blvd, Ada, OK 74820

Table 1. Oxidant Form, Stability, Stage of Development and Oxidation Potential for Oxidants Used for In-Situ Chemical Oxidation

Oxidant	Reactive Species	Form	Persistence $^{(1)}$	Stage of Development
Permanganate	MnO_4^-	powder/liquid	>3 months	developing
Fenton's	$\cdot OH, \cdot O_2^-, \cdot HO_2, HO_2^-$	liquid	minutes - hours	experimental/emerging
Ozone	$O_3, \cdot OH$	gas	minutes - hours	experimental/emerging
Persulfate	$\cdot SO_4^{2-}$	powder/liquid	hours - weeks	experimental/emerging

Oxidant and Reactions	Electrode Potential (E_h)$^{(2)}$	
Permanganate		
$MnO_4^- + 4\,H^+ + 3\,e^- \longrightarrow MnO_2 + 2\,H_2O$	1.7 V (permanganate ion)	(1)
Fenton's (H_2O_2 Derived Reactants)		
$H_2O_2 + 2\,H^+ + 2\,e^- \longrightarrow 2\,H_2O$	1.8 V (hydrogen peroxide)	(2)
$2\,\cdot OH + 2\,H^+ + 2\,e^- \longrightarrow 2\,H_2O$	2.8 V (hydroxyl radical)	(3)
$\cdot HO_2 + 2\,H^+ + 2\,e^- \longrightarrow 2\,H_2O$	1.7 V (perhydroxyl radical)	(4)
$\cdot O_2^- + 4\,H^+ + 3\,e^- \longrightarrow 2\,H_2O$	-2.4 V (superoxide radical)	(5)
$HO_2^- + H_2O + 2\,e^- \longrightarrow 3\,OH^-$	-0.88 V (hydroperoxide anion)	(6)
Ozone		
$O_3 + 2\,H^+ + 2\,e^- \longrightarrow O_2 + H_2O$	2.1 V (ozone)	(7)
$2\,O_3 + 3\,H_2O_2 \longrightarrow 4\,O_2 + 2\,\cdot OH + 2\,H_2O$	2.8 V (hydroxyl radical, see rxn 3)	(8)
Persulfate		
$S_2O_8^{2-} + 2\,e^- \longrightarrow 2\,SO_4^{2-}$	2.1 V (persulfate)	(9)
$\cdot SO_4^- + e^- \longrightarrow SO_4^{2-}$	2.6 V (sulfate radical)	(10)

[1] Persistence of the oxidant varies depending on site-specific conditions. Durations specified here are based on general observations.

[2] Reactive species in parentheses; reduction potential is negative.

Permanganate-based ISCO is more fully developed than other oxidants. Widespread use of in-situ permanganate oxidation involving a diversity of contaminants and geological environments under well-documented pilot- and field-scale conditions (in conjunction with long-term monitoring data and cost information) has contributed to the development of the infrastructure needed to support decisions to design and deploy permanganate ISCO systems. However, additional research and development is needed. Fenton-driven ISCO has been deployed at a large number of sites and involves a variety of approaches and methods involving the use of hydrogen peroxide (H_2O_2) and iron (Fe). In general, Fenton chemistry and in-situ Fenton oxidation is complex, involves numerous reactive intermediates and mechanisms, and technology development has been slower. Ozone (O_3) is a strong oxidant that has been used in the subsurface but in much more limited application than permanganate and Fenton-driven oxidation. Persulfate ($S_2O_8^{2-}$) is a relatively new form of oxidant that has mainly been investigated at bench-scale. However, considerable research and applied use of this oxidant at an increasing number of field sites is resulting in rapid development. The electrode (oxidation) potential of the oxidant and reactive species (Table 1) is a measure of the oxidizing strength of the reactive species, but is not a measure of the reaction rate with different organic compounds.

Site-specific conditions and parameters, in conjunction with oxidant-specific characteristics, must be carefully considered to determine whether ISCO is a viable technology for deployment relative to other candidate technologies, and to determine which oxidant is most appropriate. These issues and the advantages and disadvantages of each oxidant are discussed in detail.

The breadth of ground-water contaminants amenable to transformation via various oxidants is large. That is, many environmental contaminants react at moderately high rates with these oxidants. Therefore, a wide range of contaminant classes are amenable to chemical oxidative treatment (Table 2). Mixtures of contaminants may

Table 2. Assessment of the Amenability of Various Contaminant and Contaminant Classes to Oxidation Transformations

Contaminant	Oxidant																			
	MnO_4^-				Fenton's (H_2O_2/Fe)					$S_2O_8^{2-}$ (1)	$\cdot SO_4^-$ (Activated persulfate)[1]			Ozone				Ozone/ H_2O_2 (Peroxone)(2)		
	Rating sources																			
	a	b	c	d	a	b	c	d	e	a	a	b	c[3]	a	b	c	d	a	b	e
Petroleum hydrocarbons	G[4]				E[4]					G/E[4]	E[4]			E[4]						
BTEX		E[4]	E[4]	E		E	E[4]	E	E			E	E[4]		E	G[4]	E		E	E
Benzene	P[4]	G[4]	P[4]		E[4]		E[4]		E	G[4]	G/E[4]		E[4]	E[4]		G[4]				E
Phenols	G	E	E		E	E	E	E	E	P/G	G/E	E	E		E	E	E	E	E	E
PAHs	G	E	E	E	E	G	G	E	E	G	E	G	G/E	E	G	E	E		G	E
MTBE	G				G	E			E	P/G	E	E		G	E				E	E
tert-butyl alcohol						E			G			E			E				E	G
Chlorinated ethenes	E	E	E	E	E	E	E	E	E	G	E	E	E	E	E		E		E	E
Carbon tetrachloride	P	P	P		P/G	G	P		P	P	P/G		P/E	P/G	P				G	P
Chloroform		P	P			P	P		P				G/E		P				P	P
Methylene chloride			P			G	G		P				G/E		G				G	P
Chlorinated ethanes[5]	P			P	G/E			P	P	P	G/E			G			P			P
Trichloroethane[5]		P	P			E	P		P				P/E		P				E	P
Dichloroethane[5]			P			G	G		P				G/E		G				G	P
Chlorobenzene			P			E	E		E			E	E		E				E	E
PCBs	P	P	P	P	P	G	P	P	E	P	P	P	P/E		P	E	P	G	G	E
Energetics (RDX, HMX)	E				E					G	E			E						
Explosives		E	E			E	G					G	G/E		E	E			E	
Pesticides		G	G			P	P		G/E[6]			G	G/E		P	E			P	G/E[6]
1,4-dioxane[7]						E			E			E							E	E

Key: P = poor, G = good, E = excellent. While the different sources used slightly different terminology for rating the amenability, in general, they each used a three-tiered ranking represented here by the P, G, and E terminology.

Sources a, e:	P = poor, G = good, E = excellent
Source b:	P = recalcitrant, G = reluctant, E = amenable
Source c:	P = recalcitrant, no/low reactivity; G = reluctant, medium reactivity; E = amenable, high reactivity
Source d:	P = difficult to treat, E = susceptible

Notes:

[1] Persulfate/sulfate radical reactivity studies with 66 organic compounds and isomers under various conditions have been conducted elsewhere (FMC, 2005). (http://www.envsolutions.fmc.com/Klozur8482/ResourceCenter/tabid/356/Default.aspx).

[2] The reaction between O_3 and H_2O_2 produces ·OH. Therefore, the ratings from source (e) by Fenton's (H_2O_2/Fe) apply equally to the O_3/H_2O_2 (Peroxone) technology.

[3] Source (c) rated Fe-catalyzed and heat-catalyzed persulfate separately; the lower rating applies to Fe-activated and the higher rating applies to heat-activated persulfate.

[4] Benzene was rated separately from TEX or petroleum hydrocarbons; thus, the BTEX or petroleum hydrocarbons rating excludes benzene.

[5] TCA and DCA were rated separately by some sources; the other sources rated chlorinated ethanes as a class of contaminant.

[6] A detailed summary of second-order reaction rate constants between pesticides and ·OH is reported in Haag and Yao (1992).

[7] Brown *et al.* (2004) present experimental results indicating that permanganate, Fenton's reagent, persulfate, and ozone are effective in oxidizing 1,4-dioxane.

Sources:

[a] Sperry, K.L., and J. Cookson, Jr. 2002. In Situ Chemical Oxidation: Design & Implementation. ITRC Presentation to New Jersey Department of Environmental Protection, October 30, 2002. http://www.state.nj.us/dep/srp/training/sessions/insitu200210c.pdf

[b] ITRC. 2005. Technical and Regulatory Guidance for In Situ Chemical Oxidation of Contaminated Soil and Groundwater, Second Edition. Interstate Technology and Regulatory Cooperation Work Group, In Situ Chemical Oxidation Work Team.

[c] Brown, R.A. 2003. In Situ Chemical Oxidation: Performance, Practice, and Pitfalls. AFCEE Technology Transfer Workshop, February 24-27, 2003, San Antonio, TX. http://www.afcee.brooks.af.mil/products/techtrans/workshop/postworkshop03/Tuesday/pm/sourcezoneremediation/4_brown.pdf

[d] Siegrist, R.L., M.A. Urynowicz, O.R. West, M.L. Crimi, and K.S. Lowe. 2001. Principles and Practices of In Situ Chemical Oxidation Using Permanganate. 367 pp. Battelle Press, Columbus, OH.

[e] Rating based on the second-order reaction rate constants between contaminants and ·OH reported in Buxton *et al.* (1988) and Haag and Yao (1992): Excellent (>10^9 L/mol-s), Good (10^8 - 10^9 L/mol-s), Poor (< 10^8 L/mol-s).

require treatment trains involving the sequential application of technologies to accomplish the treatment objective. Chemical oxidation can be deployed under a variety of applications, i.e., in either the unsaturated or saturated zones, or possibly above-ground, and under a variety of hydrogeologic environments. In this Issue Paper, the focus is on ISCO. There are potential advantages and disadvantages of ISCO that should be assessed when considering the deployment of this technology.

Advantages:

- Applicable to a wide range of contaminants.
- Contaminants are destroyed in-situ.
- In-situ treatment may reduce costs incurred by other technologies such as pump and treat, MNA, etc.
- Aqueous, sorbed, and non-aqueous phases of contaminants are transformed.
- Enhanced mass transfer (enhanced desorption and NAPL dissolution).
- Heat from H_2O_2 reactions enhances mass transfer, reaction rates, and microbial activity.
- Potentially enhances post-oxidation microbial activity and natural attenuation.
- Cost competitive with other candidate technologies.
- Relatively fast treatment.

Disadvantages:

- Oxidant delivery problems due to reactive transport and aquifer heterogeneities.
- Natural oxidant demand may be high in some soil/aquifers.
- Short persistence of some oxidants due to fast reaction rates in the subsurface.
- Health and safety issues regarding the handling of strong oxidants.
- Potential contaminant mobilization.
- Potential permeability reduction.
- Limitations for application at heavily contaminated sites.
- Contaminant mixtures may require treatment trains.
- May have less oxidant/hydraulic control relative to other remedial technologies.

II.B. Definition

Chemical oxidation is a process in which the oxidation state of a substance is increased. In general, the oxidant is reduced by accepting electrons released from the transformation (oxidation) of target and non-target reactive species. Oxidation of non-target species, including reduced inorganics in the subsurface, also involves the loss of electrons; however, the main target during ISCO involves organic chemicals. Oxidation of organic compounds may include oxygen addition, hydrogen abstraction (removal), and/or withdrawal of electrons with or without the withdrawal of protons. The main objective of chemical oxidation is to transform undesirable chemical species into species that are harmless or nonobjectionable. For example, oxidation of trichloroethylene (TCE) and perchloroethylene (PCE) may produce reaction byproducts that include dichloroacetaldehyde and dichloroacetic acid, compounds with lower toxicity. Similarly, oxidation of phenolic compounds may produce an assortment of carboxylic acids (Huling *et al.*, 1998) that are nontoxic. Oxidation of these byproducts to CO_2 and H_2O could be accomplished through additional oxidative treatment and expense, but may not be practical for economic purposes. These reaction byproducts may also serve as microbial substrate for natural attenuation processes.

II.C. Process Fundamentals

In oxidative treatment systems, numerous reactions could potentially occur, including acid/base reactions, adsorption/desorption, dissolution, hydrolysis, ion exchange, oxidation/reduction, precipitation, etc. In environmental systems there is a wide array of reactants and conditions that influence reaction rates and pathways that vary from site to site. Often, numerous reactions are required to achieve innocuous end products, and many of the reaction intermediates are never identified. The general reactions presented in this Issue Paper represent a simplified set of reactions; however, a much broader and more complex set of reactions is expected under field conditions.

II.C.1. In-Situ Permanganate Oxidation

II.C.1.a. Chemical Reactions

Reaction 1 (Table 3) is the 3-electron half reaction for permanganate (MnO_4^-) oxidation under most environmental conditions (pH 3.5 to 12). One of the reaction byproducts is MnO_2, and in the pH range of 3.5 to 12 it is a solid precipitate. Under acidic conditions (pH <3.5), Mn in solution or in colloidal form may be present in different redox-dependent oxidative states ($Mn^{+2,\ +4,\ +7}$). Additionally, under strongly alkaline conditions, Mn may be present as Mn^{+6}. Under conditions where pH is <3.5 and >12, 5-electron and 1-electron transfer reactions occur, respectively (Table 3, half reactions 2 and 3). Reactions 1 to 3 illustrate the general permanganate reactions in the subsurface. Overall, permanganate oxidation potentially involves various electron transfer reactions (reactions 1 to 3), but is generally considered independent of pH in the range of 4 to 8.

Reactions 4 to 7 (Table 3) illustrate the oxidation of perchloroethylene (PCE), trichloroethylene (TCE), dichloroethylene (DCE), and vinyl chloride (VC), respectively. Examination of these balanced redox reactions indicate that the oxidant demand is inversely correlated with chlorine substitution. For example, the stoichiometric requirement for PCE, TCE, DCE, and VC is 1.33, 2.0, 2.67, and 3.33 mol $KMnO_4$/mol contaminant, respectively.

Although MnO_4^- will oxidize a wide range of contaminants, there are notable exceptions for compounds that are recalcitrant, including 1,1,1-trichloroethane (TCA), 1,1-dichloroethane (DCA), carbon tetrachloride (CT), chloroform (CF), methylene chloride (MC), chlorobenzene (CB), benzene, some pesticides, PCBs, and others. The rate of MTBE oxidation by $KMnO_4$ is two to three orders of magnitude slower than other oxidation processes indicating that oxidation by $KMnO_4$ limits the applicability of the process for rapid cleanup (Damm *et al.*, 2002).

II.C.1.b. Reaction Rate

Contaminant oxidation by MnO_4^- occurs by electron transfer rather than through the rapid H_2O_2 reaction and radical attack characteristic of Fenton oxidation. The relatively slow reaction rate of MnO_4^- in subsurface systems offers advantages to permanganate-driven ISCO. The slow rate of reaction allows for greater transport distances of MnO_4^- during injection delivery in medium and high permeability materials. MnO_4^- persistence in the subsurface is proportional to the concentration of MnO_4^- injected, and inversely proportional to the oxidant demand by the aquifer material and contaminant(s). MnO_4^- generally persists in the subsurface for months; however, persistence varies based on the concentration and volume of oxidant injected and from site to site. The long-term persistence of MnO_4^- contributes to diffusive transport of the oxidant into low-permeability materials, such as silty clay (Struse *et al.*, 2002a) and fractured shale (Parker, 2002). Consequently, this permits deeper penetration of the oxidant into aquifer materials that contain slow-moving contaminants.

II.C.1.c. Natural Oxidant Demand

A wide range of naturally occurring reactants other than the target contaminant(s) also react with MnO_4^- and impose a background oxidant demand. The background oxidant demand reduces oxidation efficiency and is generally greater than the demand imposed by the target compound(s). Non-target reactants mainly include organic matter and reduced chemical species (e.g., ferrous, manganous, sulfidic species). In aquifer material containing low quantities of organic carbon and reduced materials, the background oxidant demand can be low. However, under highly reduced conditions and/or organic-rich aquifer materials, the background oxidant demand can be high, suggesting that the mass and cost of MnO_4^- to achieve the treatment objectives will be high (refer also to Section III.A.3. Oxidant Demand).

II.C.1.d. Permanganate Salts

There are two forms of permanganate, potassium permanganate ($KMnO_4$) and sodium permanganate ($NaMnO_4$). Various grades of $KMnO_4$ are available from different chemical suppliers. The average prices of remediation grade $KMnO_4$ and $NaMnO_4$ are \$1.80/lb and \$6.50/lb (\$2.50/lb aqueous 40% solution), respectively. $KMnO_4$ is available as a solid that must be mixed with water before injection and is soluble at approximately 60 g/L (6%). $KMnO_4$ concentrations are generally injected

Table 3. General Permanganate Oxidation and Related Chemical Reactions

$MnO_4^- + 2\,H_2O + 3\,e^- \longrightarrow MnO_2(s) + 4\,OH^-$	(pH 3.5-12)	(1)
$MnO_4^- + 8\,H^+ + 5e^- \longrightarrow Mn^{+2} + 4\,H_2O$	(pH <3.5)	(2)
$MnO_4^- + e^- \longrightarrow MnO_4^{-2}$	(pH >12)	(3)
$4\,KMnO_4 + 3\,C_2Cl_4 + 4\,H_2O \longrightarrow 6\,CO_2 + 4\,MnO_2 + 4\,K^+ + 8\,H^+ + 12\,Cl^-$		(4)
$2\,KMnO_4 + C_2HCl_3 \longrightarrow 2\,CO_2 + 2\,MnO_2 + 2\,K^+ + H^+ + 3\,Cl^-$		(5)
$8\,KMnO_4 + 3\,C_2H_2Cl_2 \longrightarrow 6\,CO_2 + 8\,MnO_2 + 8\,K^+ + 2\,OH^- + 6\,Cl^- + 2\,H_2O$		(6)
$10\,KMnO_4 + 3\,C_2H_3Cl \longrightarrow 6\,CO_2 + 10\,MnO_2 + 10\,K^+ + 7\,OH^- + 3\,Cl^- + H_2O$		(7)

at 0.5 to 2.0% and occasionally up to 4% (40 g/L). Precipitation of $KMnO_4$ in mixing tanks, delivery lines, or in the subsurface may occur at high $KMnO_4$ concentrations and/or in conjunction with low temperatures. The simultaneous presence of VOCs and MnO_4^- in water samples is uncommon but may occur at low temperature when NAPL is present in the water sample. $NaMnO_4$ is more soluble (400 g/L; 40%) than $KMnO_4$, and is supplied as a liquid. The high concentration of $NaMnO_4$ provides flexibility in oxidant delivery to the subsurface and eliminates the potential for $KMnO_4$ granules/dust exposure during oxidant handling and mixing into solution. The density of permanganate solutions is often greater than water (1.00 g/mL). For example, $KMnO_4$ is generally injected as a 2 to 4% solution which has a density of 1.02 to 1.04 g/mL, respectively. Density-driven transport of MnO_4^- facilitates the vertical transport of the oxidant both in porous and fractured media, and enhances distribution and contact between oxidant and contaminants. This transport mechanism has been documented in several field-scale studies (Parker, 2002). $NaMnO_4$ solutions at higher concentration have even greater density and also undergo density-driven transport. The form of the oxidant ($NaMnO_4$ vs. $KMnO_4$) has little effect on oxidant consumption or filterable solids production (Siegrist *et al.*, 2002).

II.C.1.e. Impact of MnO_2(s) Accumulation

Mass Transfer: The accumulation of MnO_2(s) at the NAPL interface may interfere with mass transfer, and excessive accumulation in porous media may result in permeability reduction. A laboratory study involving visualization experiments has shown MnO_2(s) to form a rind around high DNAPL saturation zones (Conrad *et al.*, 2002; Li and Schwartz, 2004a). The DNAPL was sequestered, and a reduction both in the delivery of the oxidant and in contaminant (TCE) oxidation was measured. MnO_2(s) formed around the PCE DNAPL, and appeared to cement sand particles together forming a rock-like material with low permeability. Correspondingly, advective transport of the oxidant solution adjacent to the PCE DNAPL was reduced. Under this condition, it was proposed that diffusive transport of MnO_4^- and PCE, to and from the DNAPL, respectively, was the only transport mechanism that could facilitate chemical oxidation. In a model aquifer, MnO_2(s) deposits on or near PCE decreased both the velocity of water directly above the pool and the overall mass transfer from the remaining PCE pool (MacKinnon and Thomson, 2002). Results indicated that MnO_4^- was capable of removing a substantial mass from the PCE DNAPL pool. However, performance of ISCO as a pool removal technology will be limited by the formation and precipitation of hydrous MnO_2 that occurs during the oxidation process. In other studies, soluble chlorinated VOCs and TCE DNAPL were oxidized by MnO_4^-, and negative impacts from excessive accumulation of MnO_2(s) were not observed (Chambers *et al.*, 2000b; Struse *et al.*, 2002a).

Permeability Reduction: A few cases have been reported where a loss in permeability was attributed to excessive MnO_2(s) accumulation. Clarification of the different mechanisms and other possible causes is useful to prevent or minimize this condition. Calculations involving MnO_2(s) precipitation and deposition in aquifer pores under a wide range of conditions, including porosity (0.2 to 0.4), bulk density (1.6 to 2.13 g/cm^3), and oxidant demand (1 to 60 g/Kg), indicate that 8% or less of the voids are filled by MnO_2(s) (Luhrs *et al.*, 2006). These calculations suggest that blockage of ground-water flow by filling aquifer pores with MnO_2(s) in porous media is an unlikely explanation. Analysis of the MnO_2(s) content in aquifer core samples yielded similar conclusions (Siegrist *et al.*, 2002).

Reductions in permeability are more likely attributed to the nonuniform accumulation of MnO_2(s) in porous media due to mechanical straining, electrostatic interactions, chemical bridging, or specific adsorption. Aquifer or well-pack media near the injection point may "ripen" nonuniformly with MnO_2(s) resulting in localized high levels of MnO_2(s). Further, MnO_4^- distribution under field conditions is not uniform and also contributes to the nonuniform accumulation of MnO_2(s).

MnO_2(s) accumulation at NAPL interfaces is well-documented in lab studies (Li and Schwartz, 2000; Reitsma and Marshall, 2000; Reitsma and Randhawa, 2002); however, permeability reductions are rarely measured and reported in field studies. One explanation for this apparent discrepancy is that reductions in the permeability are localized near the DNAPL zones (Reitsma and Randhawa, 2002). Under field conditions, DNAPLs are distributed heterogeneously and screened intervals are rarely entirely completed in DNAPL-saturated porous media and may only be minimally impacted by MnO_2(s) accumulation. Permeability reductions and/or a decline in mass transfer may occur from the formation of a rind on DNAPL, as described above, but field tests and site characterization tools may be insensitive to detect the effect. However, localized DNAPL-dependent accumulation of MnO_2(s) and localized permeability reduction attributed to this mechanism may play a significant role in the mass transport and mass transfer of

MnO_4^- and VOCs, contaminant oxidation, and remediation time frames. Excessive MnO_2(s) accumulation near high DNAPL saturation areas, and the associated reduction in NAPL mass transfer described above, provides a practical explanation for contaminant rebound which is very common in source areas (refer to Section III.F.1. Untreated COCs/Rebound).

Permeability reduction may also be attributed to particulates in the injected fluids and/or gas production or injection (Luhrs *et al.*, 2006). ISCO systems that involve permanganate injection, extraction, permanganate re-amendment and re-injection may inadvertently inject suspended MnO_2(s). Assuming the extracted fluid contains oxidizable material that reacts with MnO_4^-, MnO_2(s) can form in solution before it is injected. Additionally, some MnO_4^- mixtures have high silicate content. Therefore, injecting large volumes of unfiltered oxidant solutions into a well, as in the case with injection/re-injection wells, may result in the accumulation of solids (MnO_2(s), silicates) in or near the well pack. In one study involving a 5-spot pattern where MnO_4^- was injected in a central well, and extracted in four adjacent wells, increasing injection well pressures were required to maintain constant flow (Siegrist *et al.*, 2002). Recirculation rates declined shortly after MnO_4^- injection. Although the precise cause for the fouling was not determined, re-injection of a highly concentrated TCE solution (600 mg/L) with MnO_4^- (3000 mg/L) may have resulted in the formation and deposition of MnO_2(s) within, or near the well screen and/or filter pack. The reaction of MnO_4^- in or near the well, rather than in the formation, may have prevented the dispersal of MnO_4^- and MnO_2(s) into the aquifer. Another factor which may have contributed was the high clay/silt content of the aquifer sediments in conjunction with Na^+ (i.e., $NaMnO_4$), which could have resulted in dispersed soil colloids conditions leading to a reduction in macropores and a decline in permeability. Permeability loss was also reported in another field study where horizontal well-to-well flushing of percent levels MnO_4^- was performed (West *et al.*, 1998).

$KMnO_4$ is produced as a crystalline solid that is dissolved in water prior to injection. The solubility of $KMnO_4$ is temperature-sensitive. Typical injection concentrations (2 to 3 g/L) are well below the solubility (6.5 g/L @ 20 °C). However, differences in temperature between the $KMnO_4$ solution in the mixing tank and in the aquifer could result in precipitation of $KMnO_4$ in the aquifer where it is cooler. Energy is needed to achieve dissolution of $KMnO_4$ by mixing prior to injection. If the agitation applied in the mixing process is too low or insufficient time is allowed to fully dissolve the crystalline solids, the injection solution will contain a significant quantity of $KMnO_4$(s) particles. Accumulation of these particles in the well, in the sand and gravel pack around the well, and in the formation near the well, can cause loss in permeability. Given sufficient time, the entrained $KMnO_4$(s) will dissolve into solution and the permeability can be restored. $NaMnO_4$ is highly soluble (40%; 400 g/L), produced and delivered as a solution, and only requires dilution (if desired) before injection. Therefore, precipitation of $NaMnO_4$ is not possible. At the time of this report, no documented cases were found where permeability reductions occurred at sites where $NaMnO_4$ was injected, suggesting that $KMnO_4$(s) precipitation is one probable explanation for permeability reduction.

Carbon dioxide (CO_2) is a byproduct from the oxidation and mineralization of organic chemicals and natural organic matter (rxns 4 to 7, Table 3). In column studies, permeability reduction and flushing efficiency decreased as a result of MnO_2(s) precipitation and from the formation of CO_2(g) (Li and Schwartz, 2000; Reitsma and Dai, 2000; Reitsma and Marshall, 2000; Reitsma and Randhawa, 2002). The relative mechanistic contributions of MnO_2(s) accumulation and CO_2(g) entrapment were differentiated using a pH buffering method to minimize the formation of CO_2(g) (Dai and Reitsma, 2002). In subsurface systems involving significant reaction between MnO_4^- and high concentrations of organic chemicals, large quantities of CO_2(g) can be produced in the aquifer. Due to the similarities between air sparging and CO_2(g) formation during ISCO, it is reasonable to assume that CO_2(g) entrapment may result in permeability reduction in the aquifer. For example, increased gas saturations from air sparging (generally above 20% gas saturation) can cause significant hydraulic conductivity reductions which would be detrimental to flow-through operations (Salanitro *et al.*, 2000). Therefore, CO_2(g) accumulation and entrainment in porous media could also result in blockage of ground-water flow and permeability reduction. CO_2 is soluble in water and given sufficient time, it will dissolve into solution, thus restoring the permeability. Air in the injection lines and equipment can be inadvertently injected causing a similar effect.

Increases in the permeability due to dissolution of CO_2(g) and $KMnO_4$(s) indicate that the mechanisms responsible for permeability reduction are reversible under ambient conditions. Permeability reduction can be avoided during ISCO by filtering re-injected fluids, selection of $KMnO_4$ with low silicate content, and assuring adequate mixing of $KMnO_4$ solution before injection. Redevelopment of a well may be needed to restore the permeability where the responsible mechanism is not reversible under ambient conditions. Injection of chemical reagents (organic and inorganic acids, EDTA) into MnO_2(s)-enriched aquifer material could dissolve MnO_2(s) into solution and reduce the negative impact of MnO_2(s) accumulation (Li and Schwartz, 2004a).

II.C.1.f. Metals Mobilization/Immobilization

There are two main mechanisms for increasing concentrations of metals in the ground water during ISCO: (1) the $KMnO_4$ or $NaMnO_4$ provided by the manufacturer may contain elevated levels of the heavy metals, and (2) mobilization of pre-existing redox- or pH-sensitive heavy metals (in-situ) by the oxidant. The content of heavy metals in permanganate is dependent on the type and source of the oxidant (note: $NaMnO_4$ has lower concentrations of metals than $KMnO_4$). Both forms of the oxidant are manufactured in the U.S., Germany, and China. There is only one manufacturer of permanganate in the U.S., and they provide analytical data for the heavy metal impurities in their products. Remediation grade $KMnO_4$ has been developed containing minimal quantities of metal impurities. Chromium (Cr) and arsenic (As) have historically been the impurities of concern. Due to the low maximum contaminant level (MCL) in drinking water established by EPA for these metals (0.1 mg/L total Cr MCL; 0.01 mg/L As MCL) (U.S. EPA, 2002), injection of technical grade $KMnO_4$ may result in exceeding the MCL for these elements. Generally, natural attenuation of these metals has been achieved within acceptable transport distances and time frames. Due to the possibility of exposure pathways and potential receptors, monitoring of these parameters may be needed under some conditions. A site-specific evaluation of the potential impact of heavy metals should be conducted to assess whether ground-water monitoring for these metals is needed.

Enhanced transport of pre-existing or naturally occurring redox or pH-sensitive metals may occur as a result of permanganate injection. Oxidation of Cr(III) to Cr(VI) by MnO_4^- and subsequent mobilization has been demonstrated in the laboratory (Li and Schwartz, 2000; Chambers *et al.*, 2000b). Additionally, Cr(VI) and Ni mobilization has been observed under field conditions where MnO_4^- has been injected (Crimi and Siegrist, 2003). However, Cr(VI) undergoes natural attenuation through several mechanisms (McLean and Bledsoe, 1992; Palmer and Puls, 1994), including adsorption to MnO_2(s) and various iron minerals. Several field studies have reported anomalously high post-oxidation concentrations of Cr(VI), but natural attenuation of Cr(VI) was observed (Crimi and Siegrist, 2003), and cleanup concentrations have been achieved within acceptable transport distances and time frames (Chambers *et al.*, 2000a). The potential exists at any site for metals to be introduced as an oxidant impurity, and/or pre-existing or naturally occurring metals to be mobilized by ISCO. Site conditions can provide insight into whether metals mobilization could occur including oxidant dosing, pH, buffer capacity, electrode potential (E_h), permeability, cation exchange capacity, natural metals, oxidant impurities, and local uses for the ground water (Siegrist *et al.*, 2002). Bench-scale treatability studies can be used to assess the potential significance of metals mobility, whether metals mobilization may occur under field conditions (Chambers *et al.*, 2000b), and whether attenuation mechanisms immobilize metals. Pilot-scale studies can also be used to evaluate metals mobilization and attenuation prior to full-scale implementation. Ground-water monitoring of metals may be needed to assess whether metals mobilization occurs at ISCO sites and whether attenuation is achieved within an acceptable transport distance.

MnO_2(s) behaves as a sorbent for numerous heavy metals including, but not limited to Cd, Co, Cr, Cu, Ni, Pb, Zn (Suarez and Langmuir, 1976; Fu *et al.*, 1991; McLean and Bledsoe, 1992; Siegrist *et al.*, 2002) and has been demonstrated to oxidize pentachlorophenol (Petrie *et al.*, 2002) and aromatic amines (Li *et al.*, 2003). MnO_2(s) is the primary electron acceptor for the oxidation of As(III) to the less soluble As(V) (McLean and Bledsoe, 1992). Cr(VI) adsorption and immobilization in soils is positively correlated with free iron oxides, total manganese, and soil pH (Korte *et al.*, 1976). Adsorption of metals onto Mn oxides increases with increasing pH, and is significant even under acidic conditions (Fu *et al.*, 1991). Adsorption of metals onto either Mn or Fe oxides will immobilize metals and restrict their transport in ground water. It has been reported that Cr(VI) formed and mobilized during oxidation undergoes natural attenuation within acceptable time frames and distances; however, it is not entirely clear what role MnO_2(s) has in the oxidation of Cr(III) to Cr(VI). Under some conditions, different oxides of Mn may catalyze the oxidation of Cr(III) to Cr(VI) (Nico and Zasoski, 2000). Therefore, since permanganate-based ISCO is applied under a wide range of geochemical conditions, this underscores the importance of pilot-scale testing and ground-water monitoring to assess metals mobilization.

II.C.1.g. Advantages

Numerous bench-, pilot-, and full-scale studies have been conducted resulting in a significant amount of information leading to the documentation of fundamental mechanisms and the demonstration of this technology. Considerable field experience has been obtained from the application of this technology at a wide range of sites and conditions. The chemistry involved with MnO_4^- oxidation of organic contaminants is relatively simple, and information and guidelines needed to effectively and safely inject MnO_4^- into the subsurface have been well-documented and disseminated. MnO_4^- is highly soluble, and high concentrations of the oxidant can be injected. The long-term persistence of MnO_4^- in the subsurface permits both advective and diffusive transport and can result in good distribution of the oxidant. High concentrations of MnO_4^- can result in a density greater than ground water, causing the density-driven vertical transport of the oxidant into the subsurface. This also contributes to good distribution of the oxidant, especially in low-permeability materials. MnO_4^- has been successfully delivered into a wide range of hydrogeologic environments (i.e., aquifers comprised of sands, clays, sand-clay mixtures, alluvial materials, fractured shale, fractured bedrock, etc.). Several important environmental contaminants (chlorinated ethenes) are vulnerable to oxidation, and the reaction rate between MnO_4^- and target contaminants in the aqueous and NAPL phases is fast. Short-term reduction in microbial activity results from the injection of MnO_4^-. However, this does not appear to be permanent and post-oxidation increases in microbial numbers, activity, and contaminant attenuation is often reported. Visual confirmation of MnO_4^- presence in ground-water samples and semi-quantitative analysis is possible due to the characteristic purple color of the oxidant. Considerable field experience has resulted in well established health and safety guidelines.

II.C.1.h. Disadvantages

Hydraulic short circuiting and/or preferential pathways may result in the delivery of the oxidant into non-target zones. Some important environmental contaminants are not vulnerable to oxidation by MnO_4^-. Some grades of $KMnO_4$ contain heavy metal impurities that when injected could result in unacceptable ground-water concentrations. MnO_2(s), the main reaction byproduct, may accumulate near the injection well or at the DNAPL interface (i.e., encrustment) resulting in mass transport (permeability reductions) and mass transfer limitations, respectively. Permeability reductions may also result from CO_2(g) releases. Ion exchange of Na^+ in $NaMnO_4$ for divalent cations in the aquifer matrix may result in dispersed soil colloids and contribute to permeability reductions. Permeability reduction is rarely reported and can largely be avoided by adhering to design and operational guidelines. A high background oxidant demand in aquifer and soil material attributed to naturally occurring non-target reactants may result in excessive and costly oxidant requirements. High oxidant concentrations resulting in the density-driven transport of the oxidant from the targeted zone may result in the inefficient utilization of oxidant. EPA has established a secondary maximum contaminant level for drinking water for manganese (0.05 mg/L) based on color, staining, and taste. Relatively little information is available regarding the long-term impact of the manganese residual on ground-water quality.

II.C.2. In-Situ Fenton Oxidation

II.C.2.a. Fenton and Related Reactions

In general, Fenton chemistry and Fenton oxidation treatment systems are more complex than the permanganate oxidation treatment system. This is mainly attributed to numerous reaction intermediates, side and competing reactions, phases (gas, liquid, solid, NAPL), and the numerous parameters which directly and indirectly affect Fenton-driven transformation reactions. A detailed and rigorous field demonstration of in-situ Fenton oxidation has not been conducted. Studies are needed to quantify reaction mechanisms, clarify technical issues, and optimize the treatment process. A brief summary of Fenton chemistry is presented to elucidate process fundamentals and mechanisms.

The classic Fenton reaction specifically involves the reaction between H_2O_2 and ferrous iron (Fe(II)) yielding the hydroxyl radical ($\cdot OH$) and ferric (Fe(III)) and hydroxyl ions (OH^-) (Table 4, rxn 1). Fe(III) reacts with H_2O_2 (Table 4, rxn 2) or the superoxide radical ($\cdot O_2^-$) (Table 4, rxn 3) yielding Fe(II). This general sequence of reactions continues to occur until the H_2O_2 is fully consumed. Since H_2O_2 injected into the subsurface reacts with many chemical species other than Fe(II), this technology is often referred to as catalyzed hydrogen peroxide (CHP).

$\cdot OH$ has an unpaired electron making it a highly reactive, nonspecific oxidant (Table 4, rxns 4 and 5). Correspondingly, quasi steady-state concentrations of $\cdot OH$ in Fenton systems are very low (10^{-14} to 10^{-16} M) (Huling *et al.*, 1998; 2000; 2001). Due to the fast reaction rates of $\cdot OH$, the transport distance of $\cdot OH$ is limited to only a few nanometers. Therefore, a basic tenet of Fenton oxidation is that the contaminant, Fe(II), and H_2O_2 must be in the same location at the same time.

Nonproductive reactions are represented by the general disproportionation reaction (Table 4, rxn 6) where H_2O_2 is consumed, $\cdot OH$ is not produced, and O_2 is a reaction

Table 4. Fenton and Related Chemical Reactions

$H_2O_2 + Fe(II) \longrightarrow Fe(III) + \cdot OH + OH^-$	(1)
$H_2O_2 + Fe(III) \longrightarrow Fe(II) + \cdot O_2^- + 2\,H^+$	(2)
$\cdot O_2^- + Fe(III) \longrightarrow Fe(II) + O_2(g) + 2\,H^+$	(3)
$\cdot OH$ + target contaminant $\longrightarrow$ reaction byproducts	(4)
$\cdot OH + H_2O_2 \longrightarrow \cdot HO_2 + H_2O$	(5)
$2\,H_2O_2 \longrightarrow O_2 + 2\,H_2O$	(6)

byproduct (Huling *et al.*, 1998). Examples of these reactants include catalysts such as catalase, a microbial enzyme found ubiquitously in the subsurface environment, and some transition metals such as manganese. Mn cycles between oxidation states similar to Fe, but ·OH is not produced (Pardieck *et al.*, 1992).

II.C.2.b. Contaminant Transformations

A wide range of organic compounds of environmental significance have moderate to moderately high second-order reaction rate constants with ·OH, indicating fast reaction rates (Table 2). A comprehensive compilation of reaction rate constants has been published for a wide range of reactants with ·OH (Dorfman and Adams, 1973; Buxton *et al.*, 1988; Haag and Yao, 1992). Among the contaminants represented in these references are halogenated and non-halogenated volatile organics (ketones, furans), halogenated semivolatile organics (PCBs, pesticides, chlorinated benzenes and chlorinated phenols) and non-halogenated semi-volatile organics (PAHs, non-chlorinated phenols). Fenton oxidation, therefore, has potential applicability at a large number of hazardous waste sites. Compounds with double bonds are especially vulnerable to ·OH oxidation, e.g., TCE, PCE.

In general, oxidized (halogenated) compounds without double bonds are poorly reactive with ·OH, including carbon tetrachloride, chloroform, methylene chloride, 1,1,1- and 1,1,2-trichloroethane. Although Fenton oxidation may lead to complete mineralization of organic contaminants, this is usually performed under ideal laboratory conditions where process limitations have been minimized. In the subsurface environment, non-ideal conditions (discussed below) contribute to process inefficiency and incomplete mineralization. Consequently, residual concentrations of the target compound may occur, and reaction intermediates may accumulate. Reaction intermediates are commonly less hazardous than the target compound. For example, carboxylic and chloroacetic acid compounds are relatively nontoxic and may accumulate from the oxidation of 2-chlorophenol (Huling *et al.*, 2000) and TCE, respectively. Incomplete oxidation of MTBE may result in tertiary butanol (TBA), acetone, and *tert*-butyl formate (Chen *et al.*, 1995; Yeh and Novak, 1995; Huling *et al.*, 2005) which are considered less toxic than MTBE; however, they may be unacceptable in some situations. Although TBA and acetone also undergo transformation, acetone may accumulate relative to TBA because it has a lower reaction rate constant with ·OH ($1.1 \times 10^8\ M^{-1}s^{-1}$) than TBA ($6 \times 10^8\ M^{-1}s^{-1}$) (Buxton *et al.*, 1988) and is a byproduct from the oxidation of TBA and other MTBE transformation intermediates (Stefan *et al.*, 2000). The products of MTBE oxidation also include a variety of carboxylic acids (Stefan and Bolton, 1999; Stefan *et al.*, 2000) and, ultimately, CO_2.

II.C.2.c. Other Transformations

Increasing information suggests that reductive transformations in Fenton-driven oxidation systems may play a role in the degradation of heavily chlorinated and nitro-substituted compounds (Peyton *et al.*, 1995; Watts *et al.*, 1999). These reactions may be attributed to various reductants, including superoxide radical ($\cdot O_2^-$), hydroperoxide anion (HO_2^-) (rxns 1 to 3, Table 5), and possibly Fe(II). It has been reported that the perhydroxyl radical ($\cdot HO_2$) is not a significant reductant (Watts *et al.*, 1999); however, the pK_a for $\cdot HO_2$ and $\cdot O_2^-$ is 4.8, indicating that some $\cdot O_2^-$ would be present under most environmental conditions where in-situ Fenton oxidation (ISFO) is implemented.

A review of Fenton-driven reductive reactions indicates that quinones, nitrobenzenes, nitrogen heterocycles, carbon tetrachloride, and chloroform are vulnerable to superoxide radical transformation (Watts *et al.*, 1999). Many halogenated and nitro-substituted contaminants, such as PCE and nitrobenzene, react with both ·OH and reductants at near-diffusion-controlled rates; therefore, their degradation in vigorous Fenton-like reactions may proceed through parallel oxidations and reductions (Watts *et al.*, 1999). This has several important implica-

Table 5. Formation of Reductant Chemical Species in Fenton-Driven Chemical Reaction System

$\cdot OH + H_2O_2 \longrightarrow \cdot HO_2 + H_2O$	(1)
$\cdot HO_2 \longleftrightarrow H^+ + \cdot O_2^-$ ($pK_a = 4.8$)	(2)
$\cdot HO_2 + \cdot O_2^- \longrightarrow HO_2^- + O_2$	(3)

tions regarding subsurface remediation. Reductive transformations, when combined with oxidation, yield greater potential for overall contaminant transformation. For example, TCE is vulnerable to reductive transformation and ·OH oxidation ($k_{\cdot OH} = 4.2\times10^9$). The reaction byproduct, chloroacetic acid, is vulnerable to reductive transformation ($k_{e^-} = 6.9\times10^9$). It is not uncommon for hazardous waste sites to contain a mixture of contaminants vulnerable to oxidative treatment (benzene, toluene, xylene) and reductive treatment (1,1,1-trichloroethane (1,1,1-TCA), carbon tetrachloride (CT)). Under this condition, Fenton oxidation may be an effective remedial technology for the contaminant mixture. The radicals responsible for contaminant oxidative and reductive transformations are highly reactive and are nonspecific, indicating that radical scavenging may be a potential limiting factor for both reactive pathways. Site-specific tests are needed to assess the overall role of both oxidative and reductive contaminant transformations for mixed waste conditions.

II.C.2.d. Scavenging

·OH will react with naturally occurring and anthropogenic non-target chemical species present in soil and aquifer material, e.g., H_2O_2 (rxn 5, Table 4). The non-target chemical species "scavenge" ·OH which may otherwise oxidize the target contaminants. Common ground-water anions (NO_3^-, SO_4^{2-}, Cl^-, HPO_4^{2-}, HCO_3^-, CO_3^{2-}) react with ·OH (Buxton *et al.*, 1988; Pignatello, 1992; Lipczynska-Kochany *et al.*, 1995) and may be a source of treatment inefficiency. Because H_2O_2 is generally present at high concentrations in Fenton systems and has a moderate rate constant for reaction with ·OH (2.7×10^7 $M^{-1}s^{-1}$, Buxton *et al.*, 1988), H_2O_2 is itself a primary source of inefficiency in Fenton-driven systems (Huling *et al.* 1998).

II.C.2.e. O_2(g) Generation and Exothermic Reaction

In-situ Fenton oxidation involves the injection of high concentrations of H_2O_2, a chemical that is 94.1% oxygen. For example, assuming 1 mol O_2(g)/2 mol H_2O_2, there is approximately 1400 ft^3 O_2(g) (standard temperature and pressure) released from 55 gal of 50% H_2O_2. O_2(g) produced in the subsurface as a result of H_2O_2 reactions sparges the saturated zone and perfuses the unsaturated zone. Air sparging (Ahlfeld *et al.*, 1994; Hein *et al.*, 1997; Johnson, 1998) is a technology that has been rigorously investigated and shares many similarities with O_2(g) sparging that occurs in Fenton systems. A review of air sparging literature provides insight to mass transport and mass transfer mechanisms involving O_2(g) sparging resulting from ISFO systems. The production of O_2(g) in saturated porous media during ISFO may be problematic. A significant complication of air sparge wells used to intercept a ground-water plume is the decline in permeability of the formation due to entrapped air and air channels (Ahlfeld *et al.*, 1994). This could result in a 95% reduction in conductivity for many aquifers. The low permeability barrier would impede the natural gradient of ground-water flow, and could result in the flow of ground water around the sparged zone (Ahlfeld *et al.*, 1994; Rutherford and Johnson, 1996). Increased gas saturations (generally above 20% gas saturation) can cause significant hydraulic conductivity reductions which would be detrimental to flow-through operations (Salanitro *et al.*, 2000). Reduced permeability was caused by colloidal fouling and O_2(g) binding due to H_2O_2 decomposition in porous media (Weisner *et al.*, 1996). Due to the similarities between air sparging and O_2(g) sparging from injected H_2O_2, it is reasonable to assume that O_2(g) entrapment and O_2(g) channels may interfere with ground-water transport, the delivery of H_2O_2, rebound, and delayed or poor mass transfer between aqueous, NAPL, and sorbed (solid) phases (refer to Section II.C.3.b. In-Situ Application).

O_2(g) sparging can enhance volatilization of environmental contaminants from the ground water. The pressure buildup from O_2(g) production can pneumatically transport ground water and NAPL away from the treatment area and cause artesian conditions in nearby monitoring wells. Although an in-depth field investigation of gas flow blockage, mass transfer, and transport of contaminated ground water/NAPL away from the treatment zone has not been conducted, qualitative information at sites where ISFO has been implemented indicate these mechanisms have occurred.

Fenton and related reactions are exothermic, resulting in heat release and elevated temperatures during ISFO. Heat accumulation near the injection well is common due to rapid decomposition of H_2O_2 and the slow dissipation of heat. Injection wells and nearby monitoring wells constructed of PVC have melted during ISFO. Since the melting point of PVC is 200 °C, this suggests that very high localized temperatures have resulted. The elevated temperature and production of steam (100 °C) represents a safety hazard when performing ISFO-related field activities. Heat production is functionally dependent on the volume and concentration of H_2O_2 injected, the rate of H_2O_2 injection, and H_2O_2 reactants in the subsurface. Stainless or carbon steel injection and monitoring wells have been used to withstand elevated temperatures during ISFO.

II.C.2.f. Injected Reagents

Various reagents are injected during ISFO to either facilitate or enhance contaminant oxidation, including H_2O_2, ferrous Fe, acid, and stabilizers. The volume of H_2O_2 solution injected should be sufficient to fully contact the targeted zone. The H_2O_2 concentration should be optimally balanced to minimize ·OH scavenging and to provide sufficient oxidative treatment. The reaction between Fe(II) and H_2O_2 is very fast. Therefore, each of these solutions should be injected into different wells or injected separately into the same well (pulsed), but not co-injected into the same well. Due to rapid H_2O_2 reaction in the subsurface, high injection rates, shorter injection well spacing, and lower pH can improve H_2O_2 distribution. The use of other reagents (Fe, acid, stabilizers) with H_2O_2 should be based on documented and demonstrated cost effectiveness and should be evaluated on a case-by-case basis.

II.C.2.f(1) H_2O_2

H_2O_2 solutions are clear and can be mixed with water in any proportion. Field and laboratory colorimetric analysis of H_2O_2 can be performed using various methods and field kits. The concentration range using field kits are low and require significant dilution of the sample. Colorimetric methods involving higher calibration ranges involve titanium sulfate (Schumb *et al.*, 1955; Huling *et al.*, 1998) and iodometric titration (Schumb *et al.*, 1955). H_2O_2 is available throughout the U.S. and is usually produced and purchased in bulk at 35% or 50% by weight. In many early ISFO projects, H_2O_2 had been injected at or near these concentrations despite the high potential for ·OH scavenging (U.S. DoD, 1999). Injection of H_2O_2 at lower concentrations (1 to 10%) would reduce H_2O_2 scavenging, increase the volume of oxidant solution injected and, thus, the volume of aquifer contacted, and result in lower temperatures (and H_2O_2 reaction rate) at the injection well head.

There is an abundance of reactive species that will react with H_2O_2 including, but not limited to, heavy and transition metals (Ca, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Se, Mo, Rh, Pd, Ag, Cd, W, Os, Ir, Pt, Au, Hg, Pb, Bi, Po), halogens (Cl, Br, I), microbial enzymes (catalase, peroxidase), and organic matter (Schumb *et al.*, 1955). In the subsurface, a sufficient abundance of reactive species exists, mainly iron; and rapid H_2O_2 decomposition is often observed limiting the persistence of H_2O_2 to short periods (1 to 12 hours). Assuming good contact between H_2O_2 and the targeted zone is achieved, the rapid rate of H_2O_2 reaction may be considered advantageous since this leads to short-term disruption of commercial activities at the site. However, the rapid H_2O_2 reaction rate will impede H_2O_2 transport and delivery to targeted zones. The short duration of H_2O_2 in the subsurface also may prevent the diffusive transport of H_2O_2 into low-permeability materials containing contaminants.

Numerous physical and chemical differences between bench- and field-scale conditions affect the reaction rate of H_2O_2 in both systems. Therefore, it is recommended that H_2O_2 reaction rate kinetics generated from bench-scale treatability studies not be used to design injection well spacing at field-scale. The transport distance, or radial influence of H_2O_2 from the injection point, is best determined by monitoring ground water for H_2O_2 in monitoring wells during pilot-scale ISFO. This information can be used to design the radial distance between injection wells for adequate coverage during full-scale ISFO.

II.C.2.f(2) Iron (Fe)

Ferrous sulfate ($FeSO_4$) and other salts of Fe(II) have been co-injected with H_2O_2 to facilitate the Fenton reaction. The concentration of Fe(II) injected into the subsurface has generally been above background concentrations but low (e.g., 20 to 100 mg/L) relative to [H_2O_2]. Under this condition, the relative abundance of Fe(II) may contribute to ·OH production and contaminant oxidation. Due to the slow Fe(III) reduction reactions relative to the rapid Fenton reaction (i.e., Fe(II) oxidation), a less efficient and slower rate of ·OH production occurs after Fe(II) is initially reacted with H_2O_2. Consequently, one disadvantage of Fe(II) amendment is that stoichiometric quantities are required. Fe(II) is vulnerable to numerous reactions (complexation, oxidation, precipitation) which immobilize the catalyst and minimize transport distances and distribution in the aquifer. For example, Fe(II) sorption and saturation of the Fe(III) surface can occur from the high stability of the Fe(III)-O-Fe(II) interaction (Roden and Zachara, 1996). Fe(III) is an unstable form of Fe which is vulnerable to precipitation and complexation, thus becoming immobile. Fe(III) precipitates above ≈ pH 3.5 to hydrous ferric oxide (ferrihydrite) which behaves as a poor Fenton catalyst relative to the soluble form. Fe(II) is also involved in various chemical and physical reactions which may immobilize the catalyst and limit the transport distance from the injection well.

The reaction between Fe(II) and H_2O_2 is rapid, and simultaneous injection (mixing) of Fe(II) and H_2O_2 before injection or in the injection well results in the

Fenton reaction occurring in or very near the injection well. This is an inefficient use of both Fe(II) and H_2O_2 and can be dangerous.

Iron is one of the most common elements found in soils in the U.S. (average $[Fe]_{SOIL}$ = 26,000 mg/kg, n=1318) (Shacklette and Boerngen, 1984). Not all Fe present in soil and aquifer material is available for reaction with H_2O_2. Nevertheless, at many sites, there is an abundance of naturally occurring heterogeneous forms of Fe which serves as the predominant source of catalyst for the Fenton mechanism. Under low pH and/or reduced conditions, some of the total Fe may be Fe(II), which if available, could react with H_2O_2, yielding ·OH. At most sites where Fenton oxidation is carried out, naturally occurring Fe, not the Fe(II) co-injected with H_2O_2, is predominantly responsible for H_2O_2 reactions.

Reduced permeability or fouling of injection wells attributed to Fe injection may have occurred at some sites but is not well-documented. Precipitation of Fe(II), formation of colloidal Fe particles, and entrapment in the pore throats of porous media could result in a permeability reduction. For example, the simultaneous injection of H_2O_2 and Fe(II) (which is not recommended) would likely result in Fe precipitation and immobilization in or near the well screen and/or sand pack. Fe oxidation and precipitation resulting from H_2O_2 injection alone could not explain the reduced permeability observed in injection wells at a bioremediation field site (Weisner *et al.*, 1996). Colloidal clay particles mobilized during injection have resulted in permeability losses (Weisner *et al.*, 1996, and references therein).

II.C.2.f(3) Acidification

H_2O_2 stability, contaminant oxidation efficiency, and Fe solubility and availability are greater under acidic conditions (pH 3 to 4) than in the near neutral pH range (pH 6 to 8) or higher. These effects are desirable in ISFO; therefore, pretreatment via acid injection or acidification of the injected H_2O_2 solution is common. The overall Fenton-driven oxidation reaction is acid-generating, which also contributes to acidification. Most aquifer and soil materials are well buffered in the near-neutral pH range which resists acidification. Similar to H_2O_2 and Fe(II), reaction of the injected acid with naturally occurring chemicals will limit the transport distance from the injection well. Acidification of ground water is poorly documented but generally persists over a short time frame (<1 to 3 days) and rebound to background pH may occur very rapidly in well-buffered systems. At the time of this publication, no information was available which indicated long-term, post-ISFO persistence of acidic conditions. In poorly buffered systems, acidification and acid transport will be less problematic or may not be needed altogether.

Enhanced transport of some pH-sensitive metals may occur under acidic conditions. Bench-scale treatability studies can be used to assess the potential significance of metals mobility and whether metals mobilization may occur under field conditions. Ground-water monitoring at pilot- and/or full-scale ISFO sites is needed to assess metals mobilization and whether attenuation occurs within an acceptable transport distance.

II.C.2.f(4) Stabilizers

Various reagents have been injected to enhance ISFO performance. Mainly, these are intended to enhance the transport distance of H_2O_2 and Fe(II) in the aquifer. The most common H_2O_2 stabilizer involves various forms of phosphate which reduces the availability of inorganic reactants (i.e., Fe, Mn, etc.) via complexation or precipitation reactions. By design, the stabilizer itself is immobilized through these reactions and the transport and areal influence of the phosphate stabilizer may be significantly limited depending on the composition of the aquifer material. H_2O_2 degradation rates have been shown to decline in the presence of some stabilizers (Britton, 1985; Kakarla and Watts, 1997; Watts *et al.*, 1999) relative to unamended controls in laboratory studies. However, significant degradation (97%) of H_2O_2 (15 M) occurring over short transport distances (5 in, 12.5 cm) using high concentrations of phosphate (>10 g/L as P) stabilizer (Kakarla and Watts, 1997) suggests this form of stabilization may be impractical. Unsuccessful H_2O_2 stabilization in field studies from phosphate addition was attributed to microbial enzyme and Fe catalysts in the porous media (Spain *et al.*, 1989; Huling *et al.*, 1990; Hinchee *et al.*, 1991; Aggarwal and Hinchee *et al.*, 1991). Such naturally occurring enzymes, found ubiquitously and often abundant, are highly efficient in H_2O_2 disproportionation and are unaffected by phosphate stabilizers. Field-scale transport of stabilizers and their impact on H_2O_2 transport and reaction in ISFO systems have not been demonstrated.

Stabilizers also include ligands and chelators that complex Fe(II) in the near neutral pH range allowing it to remain in solution and ideally to enhance the transport distance in the aquifer. Numerous ligands have been tested in conjunction with the Fenton mechanism (Sun and Pignatello, 1993), but two ligands, nitrilotriacetate and N-(2-hydroxyethyl) iminodiacetate, appear to be most effective (Pignatello and Baehr, 1994; Pignatello and Day, 1996). Subsurface transport and effectiveness of the ligand in ISFO systems may be limited either by reaction with ·OH (Sun and Pignatello, 1993) or by sorption of the ligand to soil and aquifer material. Enhanced transport of an Fe-ligand complex was demonstrated in a soil column relative to Fe in an acidified solution (Kakarla *et al.*, 2002). In this case, a 13% reduction in the initial Fe(II) concentration (685 mg/L as Fe) occurred over 7.9 in (20 cm) column of aquifer material. One potential advantage of injecting an Fe-ligand complex into the aquifer in the near neutral pH range is to avoid the need to adjust the subsurface pH. However, while the transport distance of the Fe-ligand complex may increase, the transport of H_2O_2 can be significantly limited in the near-neutral pH range due to rapid decomposition. Field documentation of the simultaneous transport of H_2O_2 and an Fe-ligand complex, and cost information for the Fe-ligand solution, have not been reported.

Given the abundance of naturally occurring Fe, the significant limitations for Fe(II) transport, and the unproven performance and documentation of Fe and H_2O_2 stabilization in ISFO systems, it is currently unclear whether the injection of Fe(II), and the injection of stabilizers for Fe(II) and H_2O_2 during ISFO are cost-effective.

II.C.2.g. Advantages

Potential advantages of in-situ Fenton oxidation are included in Table 6.

Potential limitations of Fenton-driven oxidation, discussed below, may also be potential advantages. For example, the heat and O_2(g) released during Fenton oxidation may enhance mass transfer via the dissolution of NAPL, desorption from the solid phase, and volatilization. However, mobilization of NAPLs could increase the surface area of the NAPL for mass transfer, and the heat/O_2(g) could increase mass transfer to the aqueous phase. Several cases have been reported where post-oxidation ground-water contaminant concentrations were elevated (U.S. DoD, 1999) and could be attributed to DNAPL mobilization. Enhanced volatilization during ISFO could result in unacceptable exposure pathways and risks. However, ISFO in conjunction with a vacuum extraction system could be used to enhance the control, capture, and removal of volatile emissions, and thus prevent the dispersal of volatile contaminants in the environment. Mass transfer of contaminants is often an important limiting factor to subsurface remediation. Therefore, these enhanced mass transfer mechanisms could enhance remediation efficiency, but have not been rigorously investigated or documented.

Table 6. Potential Advantages of In-Situ Fenton Oxidation

- ·OH is a powerful nonspecific oxidant that will react rapidly with many environmental contaminants.
- Reactions involving H_2O_2 are rapid, and it generally persists for <12 hours.
- Intermediate chemical species (·O_2^-, HO_2^-) may reductively transform contaminants. Fenton oxidation could address complex mixtures of organic compounds.
- Enhanced natural attenuation may be attributed to O_2(g) and heat. Oxidized inorganics may also serve as terminal e^- acceptors (refer to Section III.F.5. Impact of ISCO on Natural Attenuation and Biodegradation).
- Low cost of H_2O_2 ($0.26/lb; $39/1000 equivalents).

II.C.2.h. Disadvantages

There are several potential limitations to Fenton-based remediation strategies which should be evaluated (Table 7). Understanding the limitations of ISFO will allow scientists and engineers to better understand the strengths and weaknesses of the technology and allow greater opportunities for improvements in the technology. Qualitative information of these limitations and mechanisms has been reported in case studies (U.S. DOE, 1997; U.S. DoD, 1999; ITRC, 2005) and is summarized as follows: post-oxidation increases in soil gas contaminant concentrations; steam production; mass flux of volatiles from wells near the injection zone; heat released, asphalt upheaval, explosions, fire; overflowing wells; post-oxidation redistribution of contaminants, etc. Several undocumented examples of excessive heat and gas releases have been reported elsewhere (Nyer and Vance, 1999). Early applications of Fenton oxidation led to these problems and occurred as the technology was developing and guidelines for design and operations were limited. Improvements in the state of the practice of ISFO over the last few years have contributed to a reduction in the number of reported problems and health and safety incidents from field applications.

II.C.3. In-Situ Ozone Oxidation

II.C.3.a. Overview

O_3 is a gas and a strong oxidant that is sparingly soluble in water and upon reaction does not leave a residual (i.e., SO_4^{2-}, MnO_2(s)) other than O_2. Analysis of dissolved O_3 in aqueous solutions can be performed using an

Table 7. Potential Limitations of In-Situ Fenton Oxidation*

- Excessive H_2O_2 decomposition via nonproductive reactions.*
- Radical scavenging.*
- Low reaction rate between some target contaminant and $\cdot OH$, $\cdot O_2^-$, HO_2^- .*
- pH modification (acidification) is problematic in well buffered aquifers.*
- Problematic delivery of H_2O_2 Fe(II), acid, and stabilizers due to reactive transport.
- Production of O_2(g) contributes to reductions in permeability. This may reduce the flow of ground water and injected reagents through the targeted contaminated zones. It also results in sparging which contributes to volatilization and redistribution of contaminants.
- Pneumatic transport of volatiles, NAPL, and contaminated ground water away from the injection point; heaving asphalt, excessive pressure.
- Incomplete oxidation and mobilization of metals.
- Excessive release of heat and elevated temperatures associated with high H_2O_2 concentrations may damage/melt PVC/plastic wells, screens and enhance volatilization, NAPL transport, H_2O_2 reaction.
- Unproven use of stabilizer reagents.
- Health and safety issues regarding release of volatiles, steam, strong oxidant solutions.

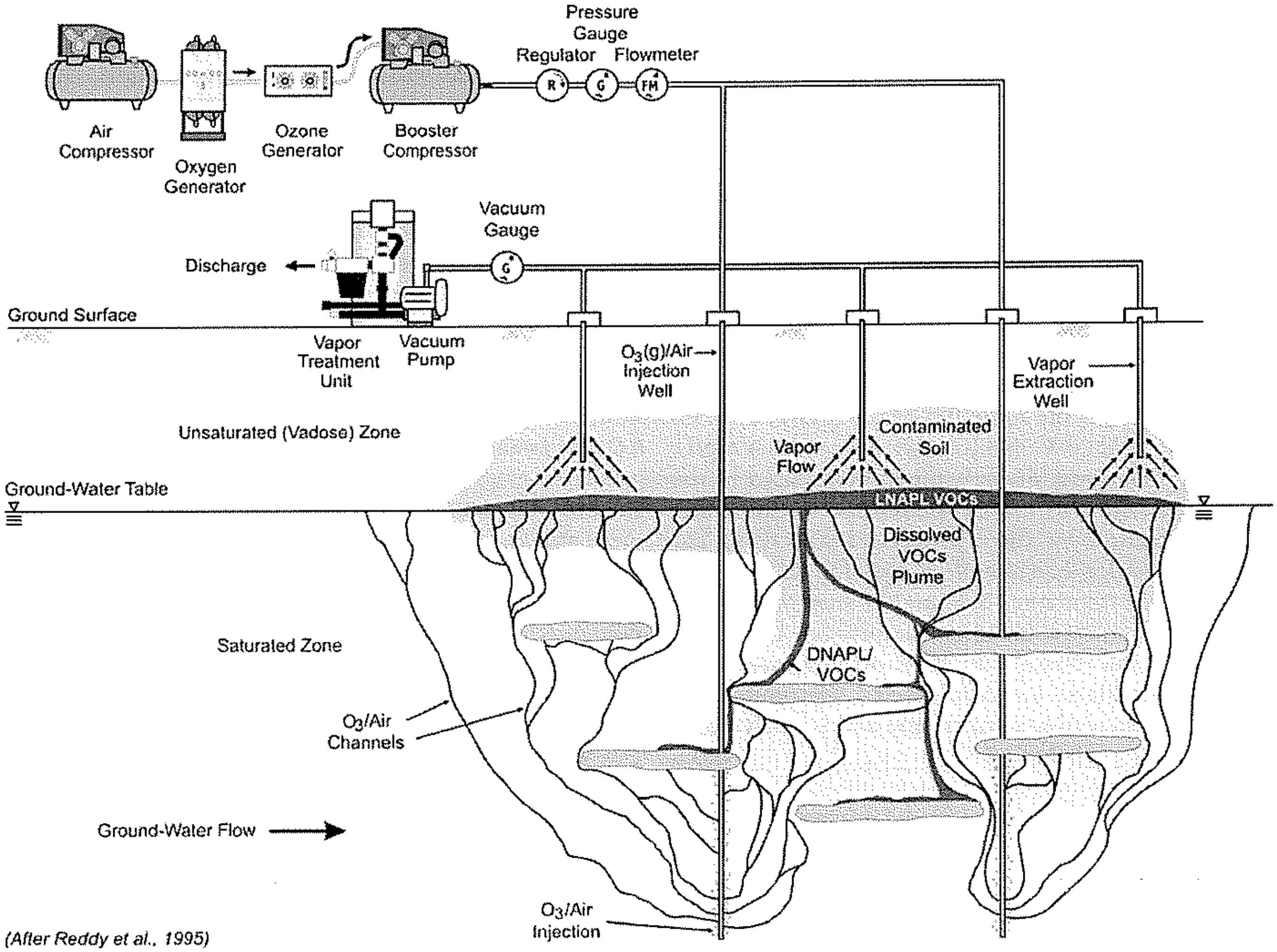
*These limitations lead to a decline in process efficiency.

indigo colorimetric method (Method No. 4500-O_3 B (U.S. EPA, 1989), APHA, AWWA, WEF, 1989) or the indigo-based HACH Ozone Accuvac Mid-range Test Kit (HACH Co., Loveland, CO). The solubility of O_3 is relatively low and is functionally dependent on temperature and the partial pressure of O_3 in the gas phase. At 1.5% O_3 by weight in air, the solubility of O_3 (pH 7) at 5 °C, 10 °C, 15 °C, and 20°C, is 11.1, 9.8, 8.4, and 6.4 mg/L, respectively. Decomposition is much more rapid in the aqueous phase than in the gas phase due to the strong catalyzing reaction by the hydroxide ion (OH^-). For example, the typical half-life of gaseous O_3 and aqueous O_3 (pH 7) at 20 °C is three days and 20 minutes, respectively. These values are based on thermal decomposition only, and no wall effects, humidity, organic loading, or other catalytic effects are considered. Decomposition increases with increasing temperature and is catalyzed by several substances including solid alkalis, metals, metal oxides, carbon, and moisture in the gas phase. Depending on the reactivity and concentration of reactants, temperature, and pH, the persistence of O_3 in the environment and the extent of contaminant oxidation will vary significantly. The instability of O_3 requires that it be generated on site. This is accomplished using a simple process where electrical generators produce O_3 from O_2(g) present in the air. Air, dry air, or O_2 is drawn into an ozone generator and the air is charged with high voltage or UV irradiation where O_2 molecules split into oxygen atoms that react quickly to form O_3. Air and pure O_2 can be used to produce O_3 concentrations of about 1% and 4 to 10%, respectively. Compression of O_3 gas is required to inject the oxidant under pressure. Under this condition, hydraulic seals and other materials used in the remedial equipment must be compatible to withstand oxidant deterioration. Teflon, Viton, and 316 stainless steel have been used for this purpose (Jensen *et al.*, 1999).

II.C.3.b. In-Situ Application

In-situ O_3 oxidation involves the injection of a mixture of air and O_3 gas directly into the unsaturated and/or saturated zones. Air sparging (Ahlfeld *et al.*, 1994; Hein *et al.*, 1997; Johnson, 1998; Brooks *et al.*, 1999) is a technology that has been rigorously investigated and shares many similarities with O_3 sparging and provides insight to mass transport and mass transfer mechanisms with in-situ O_3 sparging, which has not been rigorously investigated in subsurface systems. Injection of air beneath the water table promotes volatilization, supplies oxygen for aerobic degradation, and may induce ground-water mixing (Johnson, 1998). In addition to these benefits of air sparging, oxidative transformations also occur during O_3 sparging. Soil vapor extraction is commonly used to capture volatile emissions in the unsaturated zone during air sparging and should also be an important consideration and design component in in-situ O_3 sparging. Air sparging, in general, does not result in a uniform distribution of air bubbles extending radially from the injection well. Rather, air sparging results in the formation of a limited number of air channels in which the majority of the injected air is transported. In an ideal system, as the air moves upward due to buoyancy and outward due to applied pressure, the air channels form a V-shaped network of interconnected air channels (Elder and Benson, 1999, and references therein). Most sites are characterized as nonideal systems where air channels are heterogeneously distributed, difficult to characterize and predict (Ahlfeld *et al.*, 1994; Hein *et al.*, 1997), and allow the air to bypass a significant cross-section of the aquifer into which it is injected. This conceptual model is illustrated for an O_3 sparging system in Figure 1. During air sparging, air bubbles form in coarse-grained size porous media and air channels form in fine-grained size porous media (Brooks *et al.*, 1999; Elder and Benson, 1999). Since the majority of remedial sites are composed of media smaller than coarse sand, air channels should prevail (Brooks *et al.*, 1999). Buoyancy forces on the bubble introduce a vertical transport component which restricts the lateral transport of bubbles. Coalescing of small bubbles forms larger bubbles and eventually a continuum of gas (air channel) in the saturated media. O_3 sparging in the subsurface is analogous to air sparging, and therefore, it is reasonable to assume that the transport and distribution processes are similar.

It is generally assumed that mass transfer of volatile organics from the aqueous phase to the gas phase occurs by diffusion very near the air channels at a rate that is



(After Reddy et al., 1995)

Figure 1. General conceptual model of in-situ ozonation in the saturated zone with soil vacuum extraction to capture volatile emissions and O_3(g). On-site O_3 generation and injection into the ground water results in oxidation of ground-water contaminants and other reduced chemical species. O_3/air sparging results in the formation of O_3/air channels which contact a small cross-section of the aquifer. Close spacing of injection wells is required to accomplish a high density of air channels for adequate distribution of the oxidant.

rapid in comparison to removal in water-saturated regions around the channels (Johnson, 1998). It is reasonable to assume that contaminant oxidation occurs by similar mass transfer mechanisms, (1) the diffusion and volatilization of contaminants into the air/O_3 channels where gas-phase oxidation reactions occur, and (2) the diffusion of O_3 into the aqueous phase where contaminant oxidation reactions occur. In one air sparging study, mass transfer was restricted to a zone very near the air channel. The results indicated that for remediation to be successful, air channels during sparging must be as close as possible where mass transfer zones overlap each other. The concentration of VOCs just outside the mass transfer zone remained fairly constant (Braida and Ong, 2001). Low O_3 content in the injected air and the abundance of non-target reactants also contribute to process inefficiency. Air/O_3 channel density is related to the rate of remediation; the greater the density of air channels achieved during in-situ O_3 sparging, the greater the mass transfer and rates of reactions will occur between O_3 and contaminants in the aqueous and gas phases.

The radius of influence in the context of air sparging is ambiguous because air channels are not uniformly or radially symmetric about a sparge injection point. Further, heterogeneously distributed air channels leave large volumes of water in between the air channels untouched by the air stripping (volatilization) mass transfer mechanisms (Ahlfeld *et al.*, 1994). Again, drawing similarities between air sparging and O_3 sparging, it is reasonable to assume that treatment is not uniform (i.e., same rate of remediation) between wells where sparging (air channels) is observed. Few O_3 sparging cases actually report monitoring data for dissolved O_3 in the ground water or for sparging activity observed in wells. Therefore, the loosely defined radius of influence for in-situ O_3 oxidation is not well-documented.

Due to the low dissolved concentrations of O_3 in the ground water and poor transport of O_3 bubbles, long-term delivery of O_3 into the saturated zone is required for sufficient O_3 mass delivery. The concentration of O_3 in the ground water can be used to assess the radius of influence of injected O_3. At the time of this publication, no case study or examples were available that demonstrated the radius of influence or the transport distance of dissolved O_3 or O_3 microbubbles in ground water.

The transport of O_3 gas in unsaturated porous media is impacted by various parameters. The water content, soil organic matter, and metal oxides were found to be the factors most influential in the fate and transport of gaseous O_3 in unsaturated porous media (Choi *et al.*, 2002). The higher the water content, the faster the breakthrough. This was attributed to less contact with the metal oxide and organic matter reactants associated with the solid phase material. Nevertheless, O_3 was readily delivered and transported through unsaturated porous media where phenanthrene and diesel range organics (C_{10} to C_{24}) were oxidized.

II.C.3.c. Ozone Demand

The O_3 demand was measured in the laboratory for four different soil materials (Table 8). In this study, it was shown that increasing the water content of the soil material resulted in greater O_3 demand due to dissolution into water (probably due to the strong catalyzing reaction by OH^-) and subsequently, self-decomposition. The water content under field conditions varies considerably,

Table 8. O_3 Demand and Energy Costs to Meet the Demand of Uncontaminated Geological Material (Masten and Davies, 1997)

Geological Material	O_3 Demand (mg O_3/g soil)	Energy Cost/Ton kWh [1]	$ U.S. [2]
Ottawa sand	<0.04	<0.22	<0.013
Wurtsmith AFB, Oscoda, MI	0.022 to 0.215 [3]	<4.3	<0.26
Metea subsoil, E. Lansing, MI	1.4	31	1.85
Borden sand, Borden AFB, Ontario	2.0	44	2.64

[1] Based on energy cost for O_3 generation of 10 kWh/lb
[2] Based on a cost for electricity of $0.06 per kWh
[3] 0.022 mg O_3/g at 3.2% moisture content, 0.215 mg O_3/g at 6.8% moisture content

especially near the water table, which will strongly influence O_3 transport, O_3 demand, and costs (refer to Section III.A.3. Oxidant Demand).

II.C.3.d. Contaminant Transformations

Environmental contaminants can be oxidized either by direct reaction with O_3, or indirectly via O_3 decomposition and formation of the hydroxyl radical (·OH), a stronger oxidant (Hoigne and Bader, 1976; 1979a; 1979b) (Table 9). O_3 reacts rapidly with electron-rich olefins and aromatic compounds. Increasing chlorine substitution will decrease the rate constant of O_3 addition to olefins, and in the case of TCE and PCE, the rate constants are already so low that at short reaction times common in treatment processes there is very little destruction (Dowideit and von Sonntag, 1998). PCE reacts so slowly that it cannot be oxidized by a direct O_3 reaction within a day, and TCE will react only during extended O_3 treatment (Hoigne and Bader, 1979a). In contrast, DCE and vinyl chloride react quickly (Clancy *et al.*, 1996) due to the free C=C double bond. The reaction rate of benzene is low, requiring hours for its oxidation even at high O_3 concentration. However, the rate increases with increased substitution of functional groups that elevate the electron density of the ring (e.g., phenols, chlorophenols). Aliphatic alcohols, aldehydes, and organic acids generally react so slowly that the reaction rates are of little interest. However, formic acid, in the ionic form as formate ion, can be oxidized rapidly. NH_3 and amines show an appreciable reaction rate when in the non-protonated form. During ozonation, only those functional groups of contaminants which are especially reactive towards an electrophylic reactant (i.e., O_3), (non-halogen-substituted olefinic compounds, phenols and phenolate ions, PAHs, non-protonated amino groups, thio compounds, etc.) can be easily oxidized directly by O_3. Only the more reactive ·OH may attack molecules containing less reactive functional groups, such as aliphatic hydrocarbons, carboxylic acids, benzene, chlorobenzene, nitrobenzene, perchloroethylene or trichloroethylene (Hoigne and Bader, 1979b). Ozone has been used for PAHs (Masten and Davies, 1997; Cambridge and Jensen, 1999; Wheeler *et al.*, 2002), BTEX (Black, 2001), MTBE (Black, 2001), and chlorinated compounds such as PCE, TCE, and DCE (Masten and Davies, 1997). Pyrene and phenanthrene degradation was greater than 90% in one hour in a loamy sand soil, while degradation of 100 mg/kg chrysene was 50% in four hours (Masten and Davies, 1997).

Table 9. General Ozone Oxidation and Related Chemical Reactions

Direct Oxidation

$$O_3 + C_2HCl_3 + H_2O \longrightarrow 2\,CO_2 + 3\,H^+ + 3\,Cl^- \qquad (1)$$

·OH Formation

$$O_3 + H_2O \longrightarrow O_2 + 2\cdot OH \quad \text{(Slow)} \qquad (2)$$

$$2\,O_3 + 3\,H_2O_2 \longrightarrow 4\,O_2 + 2\cdot OH + 2\,H_2O \quad \text{(Fast)} \qquad (3)$$

The addition of H_2O_2 to O_3 in water generates ·OH, thereby increasing the oxidative capabilities of the treatment system (Table 9). Increased rates of contaminant oxidation have been reported for MTBE (Mitani *et al.*, 2002) and TCE and PCE (Glaze and Kang, 1988; Clancy *et al.*, 1996) when O_3 is combined with H_2O_2. At the time of this publication, no information was obtained where O_3 and H_2O_2 were co-injected into the subsurface in an ISCO treatment system.

II.C.3.e. Other Considerations

In-situ ozonation may involve feasibility testing (bench-scale testing) to assess whether the target contaminants can be oxidized under site-specific conditions using reasonable quantities of O_3, without deleterious side effects, such as metals mobilization or unacceptable reaction byproducts. Determination of in-situ ozone design parameters can be determined through pilot-scale testing. For example, O_3 distribution can be measured to assess whether a sufficient quantity of O_3 can be produced and delivered throughout the targeted zone. Additionally, a decline in contaminant concentration and an increase in reaction byproducts (i.e., CVOCs and Cl^-) can be measured to assure that the treatment objectives can be achieved and volatilization is not a significant loss mechanism. Fugitive O_3 emissions during production or injection may represent unacceptable risks to human health and to the environment. Where SVE is needed to capture the off-gas from O_3 injection, a nickel catalyst is used to decompose O_3. Engineering and safety controls are, therefore, required to prevent unacceptable exposure pathways. In addition, high O_2 content in confined spaces may represent unacceptable health and safety conditions and should also be monitored and managed. For example, monitoring air quality across the site should assure that the O_3 concentrations meet OSHA requirements. The delivery of O_3(g) into the subsurface may displace volatile organics from the injection zone. Consequently, control of fugitive volatile emissions may be necessary if unacceptable exposure pathways are predicted or determined. A vapor extraction system can be used to enhance the radius of influence of the O_3 and to capture volatile organics and unreacted O_3 (Jensen *et al.*, 1999).

II.C.3.f. Advantages

O_3 reacts with many, but not all important environmental contaminants. Advantages of in-situ ozonation in the unsaturated zone relative to the saturated zone include: higher concentrations of O_3 can be injected, O_3 is more stable in gas than in water, diffusive transport is greater, and higher velocities (mass delivery rates) can be achieved. Co-injection and reaction of H_2O_2 and O_3 can yield $\cdot OH$, a strong, nonspecific oxidant. However, no information was available regarding the demonstration and documentation of this co-injection process.

II.C.3.g. Disadvantages

O_3 has a short retention time in the subsurface because it reacts rapidly with a wide range of naturally occurring non-target chemical species (reduced minerals, organic matter, etc.), including the hydroxide ion (OH^-). O_3 has a relatively low solubility in water and is highly vulnerable to hydraulic short circuiting as a gas in the unsaturated zone. Based on similarities between air sparging and O_3 sparging, it is reasonable to conclude that O_3 bubbles injected into the saturated zone are poorly/nonuniformly distributed and are transported very short distances. Transport and distribution of $O_3(g)$ in the saturated zone is most likely restricted to very short distances from the gas channels (i.e., $O_3(g)$, $O_2(g)$) that form in the subsurface. Consequently, O_3 mass transport and mass transfer limitations are likely to be significant. On-site generation and compression of the corrosive O_3 gas is required to inject under pressure in the saturated zone and results in the rapid deterioration of remediation piping and plumbing materials if incompatible materials are used. Specialized oxidant-resistant materials are likely to be required. Enhanced volatilization of contaminants may result from sparging the ground water with $O_3(g)$ and $O_2(g)$. Since volatile organics and O_3 both represent a threat to human health, collection of volatile emissions (off-gases) using a vacuum extraction system may be required to minimize potential exposure pathways. O_3 does not react at an appreciable rate with some important environmental contaminants.

II.C.4. In-Situ Persulfate Oxidation

II.C.4.a. Physical and Chemical Characteristics and Chemical Reactions

Persulfate is the newest form of oxidant currently being used for ISCO. Persulfate salts dissociate in aqueous solutions to form the persulfate anion ($S_2O_8^{2-}$). $S_2O_8^{2-}$ is a strong oxidant and can degrade many environmental contaminants, or it can be catalyzed with various reactants to form the sulfate radical ($\cdot SO_4^-$), a more powerful oxidant. Catalysis of $S_2O_8^{2-}$ to $\cdot SO_4^-$ can be achieved at elevated temperatures (35 to 40 °C), with ferrous iron (Fe(II)), by photo (UV) activation (Table 10, rxns 1 to 3), with base (i.e., elevated pH), or with H_2O_2. In addition to Fe, other general activators include the ions of copper, silver, manganese, cerium, and cobalt (Liang *et al.*, 2004a, and references therein). Persulfate-driven oxidation by $\cdot SO_4^-$ has a greater oxidation potential (2.6 V) than $S_2O_8^{2-}$ (2.1 V) (Table 1) and can degrade a wider range of environmental contaminants at faster rates. Formation of $\cdot SO_4^-$ may initiate the formation of $\cdot OH$ (rxn 4, Table 10) and a series of radical propagation and termination chain reactions where organic compounds can be transformed (Huang *et al.*, 2002, and references therein).

Table 10. General Persulfate Oxidation and Related Chemical Reactions

$S_2O_8^{2-} \xrightarrow{\text{heat}} 2\cdot SO_4^-$	(1)
$S_2O_8^{2-} + Fe^{+2} \longrightarrow Fe^{+3} + \cdot SO_4^- + SO_4^{2-}$	(2)
$S_2O_8^{2-} \xrightarrow{hv} 2\cdot SO_4^-$	(3)
$\cdot SO_4^- + H_2O \longrightarrow \cdot OH + HSO_4^-$	(4)
$\cdot SO_4^- + Fe^{+2} \longrightarrow Fe^{+3} + \cdot SO_4^- + SO_4^{2-}$	(5)

The solubility of potassium persulfate is too low for environmental applications, and the reaction of ammonium persulfate will result in an ammonia residual, an undesirable reaction product. Therefore, sodium persulfate ($Na_2S_2O_8$) is the most common and feasible form used in ISCO. Sodium persulfate costs approximately $1.20/lb (Brown and Robinson, 2004). The solubility of $Na_2S_2O_8$ is high (73 g/100 g H_2O @ 25 °C) and the density of a 20 g/L solution (1.0104 g/mL) (FMC, 2006) at 25 °C is greater than water. Therefore, the density-driven transport of a high concentration solution of $Na_2S_2O_8$ would occur in the subsurface. Persulfate is more stable in the subsurface as compared to H_2O_2 and O_3 (Huang *et al.*, 2002), and can persist in the subsurface for weeks, suggesting that the natural oxidant demand for persulfate is low. The persulfate anion ($S_2O_8^{2-}$) is not significantly involved in sorption reactions. These characteristics make persulfate an attractive oxidant because it persists in the subsurface, can be injected at high concentrations, can be transported in porous media, and will undergo density-driven and diffusive transport into low-permeability materials.

Co-injection of persulfate and Fe^{+2} could be performed to accomplish the catalysis of $S_2O_8^{2-}$ to $\cdot SO_4^-$. The transport of Fe^{+2} in the subsurface can be problematic, as discussed previously (Section II.C.2.f, Injected Reagents). Oxidation of Fe^{+2} to Fe^{+3} by either $S_2O_8^{2-}$ or $\cdot SO_4^-$ could limit the effectiveness of either the injected catalyst or the oxidant. In one persulfate field study, naturally occurring ferrous iron was used to catalyze the persulfate anion while maintaining slightly reduced conditions and soluble Fe^{+2} (Sperry *et al.*, 2002). The scavenging reaction between Fe^{+2} and $\cdot SO_4^-$ (rxn 5, Table 10) and other non-target reducible reactants represents a potential sink for the sulfate radical. A balance must be achieved between adding sufficient Fe to accomplish $\cdot SO_4^-$ production and excessive Fe which may result in $\cdot SO_4^-$ scavenging (Liang *et al.*, 2004a). Scavenging of $\cdot SO_4^-$ and ·OH and a decline in the persulfate oxidation rate of MTBE were attributed to naturally occurring carbonate and bicarbonate in ground water (Huang *et al.*, 2002). The persulfate oxidation rate of MTBE decreased with increasing pH and increasing ionic strength (Huang *et al.*, 2002). However, the decline in the oxidation rate from pH 2.5 to near neutral was only 30%, indicating that persulfate oxidation is pH-dependent, but only moderately sensitive to this parameter.

II.C.4.b. Contaminant Transformations

Several environmental contaminants have been oxidized in laboratory experiments using persulfate and various catalysts. Fe^{+2}-assisted sodium persulfate oxidation of TCE (60 mg/L) removed 47% of the TCE at a persulfate: iron:TCE molar ratio of 20:5:1 (Sperry *et al.*, 2002; Liang *et al.*, 2004a). TCE oxidation also occurs via chelated Fe^{+2}-assisted treatments (Liang *et al.*, 2004b). TCE was significantly oxidized at 40 to 60 °C, and TCA at 60 °C, within several hours (Liang *et al.*, 2001; Liang *et al.*, 2003). In a field test involving a glauconitic (iron rich, 3 to 15 mg/L Fe^{+2}) sandy aquifer, persulfate catalyzed by naturally occurring ferrous iron oxidized 30 to 50% of a TCE and cis-1,2-DCE concentration of about 7 to 9 mg/L and vinyl chloride (Sperry *et al.*, 2002). Heat-assisted sodium persulfate (at about 8 g/L) oxidized MTBE in the ppm range (half-life <1 hour; 40 °C) in a buffered laboratory solution. A much slower MTBE degradation rate was observed in ground-water samples, perhaps due to radical scavenging by bicarbonate ions (Huang *et al.*, 2002). Persulfate (0.0357 mg/L; persulfate: organic matter ratio of 12 g/g; 70 °C) oxidation of PAHs (<200 mg/kg; 16 EPA PAHs) at bench-scale tests with a three-hour reaction time varied widely in 14 different soils and sediments. Loss of the 16 PAHs varied between 0 to 80%; 0 to 85% loss of 2- and 3-ring PAHs; 0 to 75% loss of 4-ring PAHs; and 0 to 70% of 5- and 6-ring PAHs (Cuypers *et al.*, 2000). The reaction between $Na_2S_2O_8$ and 66 organic compounds (and isomers) in aqueous solution at various temperatures (room temperature, 20 °C, 35 °C, 40 °C, or 45 °C), persulfate concentrations (1, 5, 11 g/L), presence of Fe^{+2} or catalyst, and time of contact (3, 14, 20, 21, 90 days) has been evaluated (FMC, 2005).

Overall, heat-assisted persulfate oxidation is rapid, and raising the temperature of aquifer material and ground water is technically feasible; however, the economic feasibility has not been established. Methods used to raise the temperature in subsurface systems include radio frequency heating, steam injection, six phase, electrical resistance, etc., but have not been demonstrated at field-scale in conjunction with persulfate oxidation.

Liang *et al.* (2001) hypothesized that sodium persulfate (being a fairly strong oxidant at ambient temperatures) could have an important role in the oxidation of soil organic carbon. If so, one potential use of persulfate in in-situ remediation would be for the oxidation of soil organic matter, prior to use of a different oxidant for oxidation of contaminants. The destruction of soil organic matter is important since it will decrease the natural oxidant demand (NOD) of the soil, allowing subsequent oxidant additions to be used more efficiently for target contaminants. However, Brown and Robinson (2004) questioned the effectiveness of persulfate for decreasing soil oxidant demand, stating that it was relatively unreactive toward naturally occurring organic matter.

II.C.4.c. Advantages

Persulfate is more stable in the subsurface than H_2O_2 and O_3, and the radical intermediate, $\cdot SO_4^-$, is more stable than ·OH. This suggests fewer mass transfer and mass transport limitations. Persulfate will react with benzene, while permanganate does not, thus allowing this form of oxidant to be used in the remediation of fuel spills and BTEX-contaminated ground water. Persulfate does not appear to react as readily with soil organic matter as permanganate (Brown and Robinson, 2004). This may not be an advantage over permanganate in aquifer material where the oxidant demand is predominantly due to reduced mineral species.

II.C.4.d. Disadvantages

In-situ chemical oxidation involving persulfate is an emerging technology and, in general, the peer-reviewed literature is limited, and there are few reports of bench-and field-scale studies. The lack of information pertaining to the fundamental chemistry and applications in subsurface systems suggests there is also a limited infrastructure of knowledge and experience upon which to design successful remediation systems. This limitation/disadvantage will diminish with time based on ongoing fundamental and applied research.

Persulfate is less stable than permanganate and will not persist as long in subsurface systems. Catalysts are required in the persulfate reaction to produce the more powerful sulfate radical. There will likely be difficulties in achieving the optimal mix of reagents (i.e., $Na_2S_2O_8$, catalysts) in the subsurface due to the lack of naturally occurring catalyst, and due to the difference in transport behavior of these reagents upon injection. $\cdot SO_4^{2-}$ scavenging is a source of process inefficiency that is currently not well understood nor documented. $Na_2S_2O_8$ costs approximately \$2.70/kg, which is more than $KMnO_4$ and H_2O_2. This cost of oxidant may be offset by the lack of oxidant demand by non-target aquifer materials.

III. TECHNOLOGY DESCRIPTION AND TECHNOLOGY SELECTION FACTORS

III.A. Bench-Scale Studies

Bench-scale treatability studies can be useful to gain insight on the feasibility of contaminant oxidation prior to field-scale applications. In complex, heterogeneous systems it is difficult to predict specific reactions, oxidation efficiency, oxidation byproducts, or whether any of the potential limitations apply. The methods and materials of bench-scale treatability studies may vary based on the oxidant used and the objectives. It is important to recognize the physical differences between bench- and field-scale systems. The use of bench-scale treatability results from simplified systems to design field-scale ISCO systems must be heavily scrutinized.

III.A.1. Objectives

One objective of a bench-scale treatability study is to establish proof of concept that the target compound can be transformed by oxidative treatment(s) given the potential limitations. Another objective in MnO_4^- bench-scale studies is to measure the oxidant demand. This data and information is used to assess the feasibility of ISCO and to assist in the design of oxidant injection at pilot- or field-scale (refer to Section III.E.2.a. Permanganate Oxidation). For all oxidants, significant contaminant reduction should be demonstrated using reasonable quantities of oxidant and reagents under reasonable simulated conditions. For example, with Fenton oxidation, the pH of the test reactors should not be conducted at the optimal pH (pH 3.5 to 4) unless the acidic condition can be accomplished at field-scale. Otherwise, the results may overestimate treatment effectiveness. Assessment of the reaction byproducts may also be an important objective since the oxidative treatment of some target compounds or complex chemical mixtures may be poorly documented or unknown. Side and competing reactions may yield undesirable byproducts. Historically, mobilization of redox- and pH-sensitive metals has been a concern and may be an important objective in the bench-scale treatability study. Although attenuation of metals generally occurs over short transport distances, this may be an important issue where high metals concentrations exist (i.e., naturally occurring or co-disposed with organics) and/or where potential receptors are nearby and could be impacted over short transport distances.

Under some conditions, bench-scale treatability studies may not be feasible. At one site underlain by a coarse alluvial aquifer, it was difficult and costly to obtain unconsolidated aquifer media using direct push or hollow stem auger. Air rotary drilling was used to install wells at the site but this method of acquiring aquifer material would significantly impact (pulverize) the physical integrity of the samples (i.e., the surface area, reactive species, redox, and contaminant concentrations would be altered significantly). Consequently, the MnO_4^- oxidant demand would be highly variable and would likely yield erroneous results that would confuse the feasibility assessment. A small field-scale pilot treatability study was conducted which was designed to limit cost and to assess the feasibility of ISCO.

III.A.2. General Guidelines

Components of the bench-scale reactor should include the aquifer material since it will contain the majority of the contaminant(s) and other parameters that will largely influence oxidant demand and the success or failure of the treatment process. Disturbed aquifer material is generally used in this procedure. Use of ground water from the site is ideal but is generally not critical. Capture and quantification of contaminant losses from the reactor is necessary to maintain a mass balance and to assess treatment performance. These losses include volatiles, displacement of aquifer material, aqueous solutions, or DNAPLs. Reactions involving H_2O_2 may release significant quantities of heat and $O_2(g)$ and enhance volatilization. Volatile losses can be captured and quantified using inert gas bags or an activated carbon trap. A nonvolatile contaminant analog can also be amended to the reaction vessel and its loss can be used to predict the oxidative transformation of the target compound (Huling *et al.*, 2000). Failure to capture volatile losses could result in an overestimate of oxidative treatment.

Recommended monitoring parameters that are a direct indicator of oxidative treatment include the target compounds, reaction byproducts, metals, and the oxidant (i.e., H_2O_2, MnO_4^-, $S_2O_8^{2-}$, O_3). Indirect indicators such as CO_2, dissolved oxygen (DO), total organic carbon (TOC), chemical oxidant demand (COD), and temperature have been used but are generally unreliable and not recommended. Control reactors can be used to help quantify non-oxidation losses and are recommended. Measuring pre- and post-oxidation concentrations of the target compound in the aqueous, solid, and gaseous phases allows mass balance calculations which serve as the basis for performance evaluation.

III.A.3. Oxidant Demand

"Natural oxidant demand" generally refers to the demand attributed to naturally occurring materials (i.e., reduced inorganic species + organic matter). The total oxidant demand includes both the natural oxidant demand and the demand due to anthropogenic contaminants. In this document, the term oxidant demand is synonymous with total oxidant demand.

The oxidant demand for H_2O_2 is not measured since H_2O_2 decomposition involves catalytic reactions (Table 4, rxns 1 to 2) and the oxidant demand would be infinite. The oxidant demand in O_3 systems may also be difficult to quantify due to reactions between O_3 and H_2O and OH^-. Under some conditions, the consumption of O_3 by these reactants may be relatively small. Four different geologic materials exerted a limited O_3 demand (Table 8), i.e., the rate of O_3 degradation in soil columns was slow after the immediate O_3 demand was met (Masten and Davies, 1997). Bench-scale measurements of the O_3 demand may successfully separate the high O_3 demand associated with reducible mineral species from a longer-term demand of lower magnitude attributed to OH^- and H_2O. However, the long-term O_3 demand under in-situ conditions has not been well-documented and may be significant.

The permanganate oxidant demand is often measured at bench-scale in batch reactors prior to field-scale applications and many variations of the test procedures have been reported. Testing procedures also include column tests (Drescher *et al.*, 1998; Mumford *et al.*, 2004) and field push-pull tests (Mumford *et al.*, 2004). A standardized method to measure the oxidant demand is under review by the American Society for Testing and Materials (ASTM) (Vella *et al.*, 2005) and can be reviewed at an EPA website http://www.epa.gov/ada/topics/oxidation_issue.html. The oxidant demand results can be used to assess the preliminary feasibility of in-situ permanganate oxidation. The test involves two tiers of testing. Tier 1 is an inexpensive, rapid (minimum 48-hour test) preliminary screening test used to estimate the oxidant demand of aquifer materials and contaminants. Tier 1 testing involves a minimum of 250 grams of soil and 250 mL of site ground water per soil sample, a minimum of 50 grams of soil per reactor vessel, 3 $KMnO_4$ loading rates (5, 15, and 30 g $KMnO_4$/kg soil), a soil:water ratio of 1:2 (wt.:wt. wet basis), and a minimum of 48 hours reaction time. Guidelines for soil sample handling (preparation, mixing, compositing, drying, storage), testing procedures (reactor vessel, MnO_4^- measurements, mixing, etc.), and oxidant demand calculations are provided.

Oxidant demand results from laboratory studies are generally used in conjunction with other site-specific treatability results to assess the preliminary feasibility of ISCO including projecting the cost for oxidant, assess technical and economic feasibility, compare ISCO with other candidate technologies, assess implementability, etc. Oxidant demand data may also be used to assist in the design of pilot- or full-scale injection systems. However, there is not a uniform approach or method used for either of these purposes (refer to Section III.E.2. General Conceptual Approach to ISCO).

Tier 2 of the proposed ASTM method is more complex and, in theory, could provide comprehensive site and testing data, including extensive sampling methodology, longer test duration, increased reaction data points, and reaction kinetics. Tier 2 is currently under development and has not yet been submitted to ASTM for review. Other guidelines for performing oxidant demand tests are also available (Haselow *et al.*, 2003), and continued development is needed.

Long-term oxidant demand testing reveals that the oxidant demand extends much longer than 48 hours, resulting in higher oxidant demand values than measured over a shorter time periods (Figure 2). The long-term persistence of MnO_4^- (>>2 days) in aquifer material has been well-documented suggesting that long-term testing may be more representative of testing conditions. This may be important in cases where contaminants persist for long periods. For example, contaminants present as NAPLs or contaminants in low-permeability materials may have

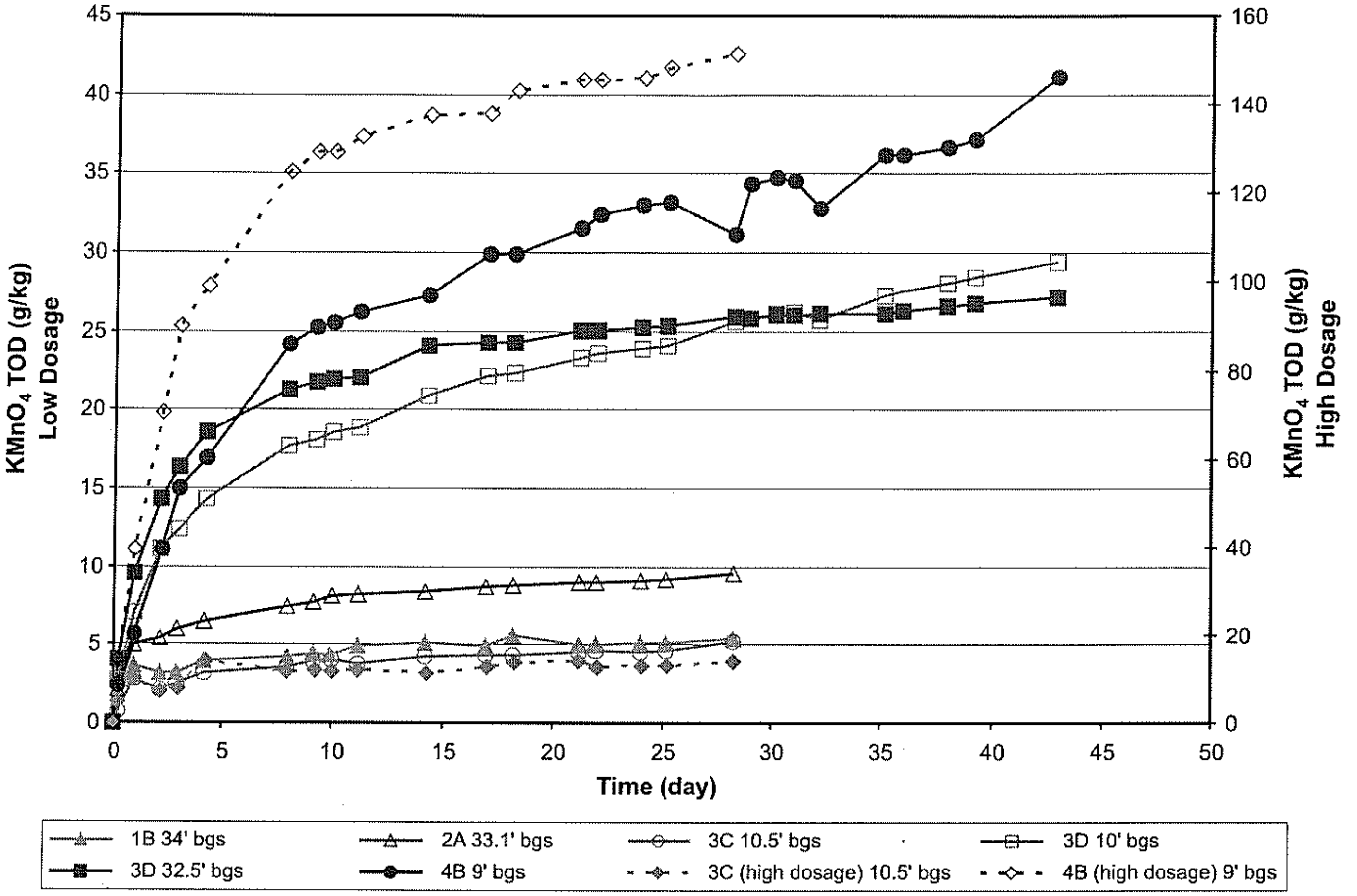


Figure 2. The total oxidant demand (TOD) was measured by amending aquifer samples (30 to 50 g dry weight) with $KMnO_4$ solutions (0.5 L; 2.1 g/L (low dosage) or 10.5 g/L (high dosage)) (Huling and Pivetz, 2003). The aquifer samples were collected in an area of approximately 50×50 ft and between 9 to 34 ft bgs. The data represent the average of two split samples at each depth and location. TOD values increase with time (28 to 44 days) and a significant difference in TOD occurs between short-term (two days) and long-term testing periods. Although replicate samples were collected from adjacent sections of the core (a few inches apart), variability in TOD (>100%) was measured in replicates at both locations 2A and 4B. Aquifer core samples 3C and 3D (shallow) were collected 10 ft apart, from the same vertical interval. However, the average oxidant demand was different by nearly a factor of 5 between locations. Further, greater oxidant demand was measured at the high oxidant dosage (4B—151 g/kg vs. 43 g/kg; 3C—14 g/kg vs. 5 g/kg). TOD values resulting from testing at high dosages for samples 3C and 4B are indicated by dashed lines and are read using the right-hand y axis.

limited contact with the oxidant. Under these mass transfer and/or mass transport-limited conditions, long-term persistence of the oxidant may be required to achieve the treatment objective. Conversely, the oxidant demand measured in long-term tests may be an overestimate when mass transfer/transport is not limited and oxidation is rapid. Long-term bench-scale tests may be used to quantify the upper value of the oxidant demand. Alternatively, results from a short-term test (such as ASTM, Tier 1) must be interpreted in a manner that considers the effects of long-term contact between oxidant and aquifer material. Continued development of standardized oxidant demand testing is needed.

The permanganate oxidant demand measured in bench-scale tests can be impacted by various parameters. Spatial variability (depth, location) in the composition of the aquifer material may affect the oxidant demand (Figure 2). Collection of aquifer samples in sufficient number at various depths and locations may be needed to represent the variability in oxidant demand. This information can be used to establish a correlation between the oxidant demand and different lithologic or geochemical zones. Since the composition of organic matter varies in sands, silts, and clays, variability in the oxidant demand will also vary. Soil with 1.6% TOC prior to oxidation had 0.6% TOC remaining after oxidation by $KMnO_4$ in a column study, indicating that organic matter will exert an oxidant demand (Drescher *et al.*, 1998). Naturally occurring organic matter exhibits various chemical compositions and therefore, fractions of organic matter may range from easily oxidizable to recalcitrant. Reduced chemical species (i.e., sulfides, ferrous Fe, manganous Mn, etc.) in subsurface media can be oxidized during ISCO and consume oxidant. Geochemical environments rich in organic matter and/or reduced mineral species may exert a significant oxidant demand. Bench-testing can be used to assess whether excessive natural oxidant demand will be exerted. The type (Table 3, rxns 4 to 7) and phase (aqueous, sorbed, NAPL) of organic contaminants will also affect the oxidant demand. Exposure of the aquifer material to air and loss of volatile organics during handling will artificially lower the measured oxidant demand. Such exposure should be minimized since this could result in an underestimate of the actual oxidant demand.

The oxidant demand is functionally dependent on the concentration of MnO_4^- used in the test (Figure 2). Under comparable conditions, the oxidant demand increases with an increase in the oxidant concentration (Siegrist *et al.*, 2002). An oxidant demand of 2.8 g $KMnO_4$/kg was measured when amended with a 500 mg/L $KMnO_4$ solution, and increased to 10.8 g $KMnO_4$/kg when amended with 5000 mg/L $KMnO_4$ (Struse *et al.*, 2002b). The concentration of oxidant most representative of actual field conditions should be used in the bench test to obtain the most accurate results. The oxidant demand is also dependent on (1) the contact time between the oxidant and soil, (2) mixing, and (3) the solids:solution ratio. The oxidant demand decreased as the solids: solution ratio increased (Mumford *et al.*, 2004). However, given sufficient time, the oxidant demand converged to a similar value regardless of the mass of aquifer material used. The maximum NOD value depends only on the mass of oxidizable matter and the stoichiometry between that oxidizable matter and the oxidant, and that it does not depend on the mass of aquifer material (Mumford *et al.*, 2004). In summary, for short reaction periods, the solids:solution ratio is likely to have a significant effect on the results; for longer reaction periods, the solids:solution ratio is likely to be less important.

The objectives and guidelines presented for permanganate bench-scale testing are also applicable to persulfate. For example, in soil slurry laboratory experiments, the soil with the lowest fraction of organic carbon (f_{oc}) had the highest TCE and TCA oxidation efficiency by sodium persulfate (Liang *et al.*, 2001). In general, the persulfate oxidant demand is lower than the permanganate oxidant demand, suggesting that lower oxidant loading may be required.

III.B. Pilot-Scale Studies

Pilot-scale treatability studies provide useful information to help design and plan full-scale ISCO implementation. Specifically, due to the spatial variability of samples collected and used in bench-scale tests, pilot-scale studies can provide data and information from the oxidative treatment over a larger aquifer volume. The methods and materials of the study may vary based on the oxidant used and the objectives.

III.B.1. Objectives

The objectives may include the following: determine the injection rate vs. injection pressure; assess various injection strategies; assess the travel times, distribution (vertical/horizontal), and persistence of the oxidant and reagents (Fe, acid, stabilizers, chelators); determine whether ground-water contaminants are mobilized or are volatilized; assess the mobilization of metals; assess contaminant rebound; determine reaction byproducts; conduct a preliminary performance evaluation of contaminant oxidation; assess the adequacy of the monitoring program; anticipate well fouling problems; and assess the potential difficulties in scaling up a treatment system. Multiple injections of oxidant and/or reagents under different conditions can be used to accomplish different treatment and testing objectives.

III.B.2. General Guidelines

A detailed assessment of ISCO performance evaluation and rebound generally requires extended periods of time due to the slow mass transfer and mass transport processes in conjunction with the slow rate of ground-water movement. Additionally, in Fenton systems, a significant disturbance results from H_2O_2 injection and the subsequent release of heat and $O_2(g)$. It is common to see significant increases in total dissolved solids in ground-water samples collected soon after H_2O_2 injection. Therefore, the ground-water quality is highly disturbed (transient) and requires an extended period of time to approach chemical equilibrium. Both the detailed and general information acquired through the pilot-scale study can be used to help design and plan subsequent injection events. Monitoring data and information are useful to design the monitoring system for the full-scale system including appropriate locations and depths of monitoring wells and appropriate monitoring parameters and frequency.

The following general guidelines for ISCO pilot-scale studies are applicable for all oxidants, and also apply to full-scale implementation. Conceptually, an outside-in injection strategy involves initial oxidant injections on the periphery of the known contaminant zone. Subsequent injections in the middle of the source zone may transport contaminants into adjacent zones already containing oxidant and/or contaminants. Ideally, this reduces the transport of contaminants from the source zone into uncontaminated areas. Ground-water samples represent an integrated measure of contaminants present in the subsurface and provide valuable insight regarding performance evaluation from the oxidative treatment. However, due to the slow mass transfer and mass transport processes which occur in the subsurface, sufficient time should be allowed (after ISCO is performed) before ground-water samples are collected for performance evaluation. Assuming potential receptors are located close to the injection area, an expedient ground-water monitoring program (rapid turn-around) may be needed. Soil core samples may provide immediate feedback on performance, but variability in contaminant concentrations may require that numerous soil core samples be collected to minimize uncertainty and allow for an accurate assessment of treatment performance. Aquifer samples can be highly effective in performance evaluation where contaminants (i.e., DNAPL) have accumulated at distinct lithologic units and contaminant distribution is more easily defined.

Pilot- and full-scale ISCO should be implemented in a manner that recognizes and minimizes the transport of contaminated ground water or NAPLs from the source area into low contamination/clean areas. Pilot-scale studies are sometimes deployed in or downgradient from a source zone. In this case, it can sometimes be difficult to distinguish between rebound and upgradient flushing of contaminants into the study area. An outside-in approach can be used to help minimize this complication (i.e., a wedge that extends from the upgradient edge to the central area of a source zone). Contaminant transport from upgradient of the remediated area and possible recontamination underscores the need to design the oxidant delivery system for full coverage.

In-situ oxidant push-pull tests may be used to evaluate the permanganate oxidant demand (Mumford *et al.*, 2004), and presumably persulfate oxidant demand, over relatively large aquifer volumes. This involves the injection and recovery of a solution containing an oxidant and a conservative tracer. Measurement of oxidant demand is determined from the analysis of the recovery breakthrough curves of the oxidant and tracer. There are some design and operational limitations of this technique, but potentially it could be used with existing monitoring wells and may provide accurate oxidant demand data.

III.C. Technology Applicability

III.C.1. Location of Oxidant Application

III.C.1.a. Saturated Zone

ISCO involving MnO_4^-, Fenton's, O_3, and $S_2O_8^{2-}$ has predominantly been applied in saturated, unconsolidated, highly contaminated (source zone) porous media at hazardous waste sites (refer also to Section III.F.5 Oxidant Delivery). The injection of O_3 gas into the saturated zone has been used but is vulnerable to nonideal transport mechanisms including preferential pathways (refer to Section II.C.3.b. In-Situ Application). Few scientific investigations of in-situ persulfate oxidation have been reported; however, numerous studies are underway and it is anticipated that more information will soon become available regarding $S_2O_8^{2-}$. Presumably, persulfate oxidation will be applicable to both the saturated and unsaturated zones, similar to permanganate.

Environmental contaminants present either as a NAPL, adsorbed onto aquifer material, or in the aqueous phase (dissolved) are all vulnerable to chemical oxidation transformations. Due to competition by naturally occurring non-target reactants in the aquifer material, the most efficient use of chemical oxidation occurs where the concentration of the target contaminants is highest. The *oxidation efficiency* (η), defined as mass of contaminant transformed/mass oxidant reacted, is highest in source zones. Therefore, the most cost effective contaminant oxidation occurs in source zones. This is consistent with the common remedial objective that initially targets the source zone(s) at a site. The downgradient contamination plume is often a secondary priority and may not involve ISCO due to the large area of contamination relative to the source area, lower oxidation efficiency, and greater cost.

ISCO is not commonly applied in the ground-water plume extending downgradient from the source zone. This trend is mainly attributed to the small size of source zones compared to the downgradient plume. In the source zone, the oxidant can be applied at high concentration, focused in specific source area locations, and can achieve greater oxidation efficiency relative to downgradient zones. Under this set of conditions, larger quantities of contaminant can be transformed using lower quantities of oxidant and at lower cost. However, treatment objectives vary between sites. The treatment objective in some cases is to prevent the off-site migration of contamination. Given this objective, periodic applications of MnO_4^- have been used to form a downgradient (oxidation) barrier to oxidize ground-water contaminants migrating into the treatment zone. Under this condition, the oxidation efficiency is expected to be lower relative to the source zone due to lower concentrations of contaminants.

Despite the lower oxidation efficiency expected in downgradient (non-source) zones, it is estimated that the oxidant demand required to meet the treatment objective may not be as high compared to source zone applications. Mass transfer and mass transport limitations between MnO_4^- and NAPLs, and between MnO_4^- and high concentrations of sorbed contaminants require longer residence times of the oxidant and consequently higher oxidant demand. Fewer limitations occur between MnO_4^- and soluble contaminants, resulting in faster oxidation, shorter oxidant residence times, and a lower oxidant demand. Therefore, at least in theory, lower concentrations of oxidant and fewer applications are required to meet the treatment objective. Oxidation of soluble contaminants in low-permeability materials require longer residence times for diffusive transport and will result in a higher oxidant demand relative to more permeable aquifer materials.

ISCO is more often used in unconsolidated porous media than in fractured media. This is partially attributed to a greater number of hazardous waste sites in unconsolidated porous media and more in-depth knowledge of the flow system. In-situ permanganate oxidation has been carried out in fractured shale (Parker, 2002) and fractured bedrock. Fenton oxidation has significant limitations in fractured systems due to significant differences between the reaction and the transport rates of H_2O_2. Specifically, contamination in fractured media may be found in both the primary porosity (matrix) and in the secondary porosity (fractures). The volume of matrix porosity is generally greater (10 to 1000×) than fracture porosity. Therefore, the mass of contamination contained within the matrix porosity is potentially much greater than in the fracture porosity. Transport of contaminants, O_3, H_2O_2, and Fe^{+2} within the matrix porosity is predominantly by diffusion. Due to the rapid rates of reaction of O_3, H_2O_2 and Fe^{+2} relative to diffusive transport, there is insufficient time for the oxidant and reagents to penetrate the contaminated media. Consequently, O_3, H_2O_2, and Fe^{+2} transport is restricted mainly to fracture porosity, the contaminants predominantly reside within the matrix porosity, and poor contact occurs between the oxidant, reagents, and the contaminant. Although poorly documented, a few unsuccessful attempts of Fenton-driven oxidation in fractured systems have occurred. No cases were found where O_3 or $S_2O_8^{2-}$ was injected into fractured media.

III.C.1.b. Unsaturated Zone

ISCO is less frequently used in the unsaturated zone than in the saturated zone. The delivery of permanganate solution into the unsaturated zone has occurred via a variety of methods including, but not limited to, application to surface soils, emplacement into trenches/excavations, former surface impoundments, deep soil mixing, and injection into hanging wells/injectors (screened in the unsaturated zone). Similar to the saturated zone, direct push injection over short screened intervals, at least in theory, could be used to deliver the permanganate solution into the unsaturated zone. Presumably, the injection of persulfate and permanganate solutions would be similar; however, no reports were found describing persulfate application in the unsaturated zone.

Conceptually, due to the slow reaction rate of permanganate and persulfate, vertical transport of the injected oxidant solution would result in the delivery of the oxidant to areas underlying the injection zone. Due to the lack of buoyancy forces, the rate of vertical transport in the unsaturated zone would be greater than in the saturated zone. Most subsurface systems exhibit some degree of anisotropy where the ratio of horizontal to vertical conductivity is 10 or greater. Under this condition, vertical transport could require long residence times of the oxidant. This suggests that the fast reaction rate of H_2O_2 would result in short vertical transport distances and poor distribution within the unsaturated zone.

In-situ O_3 oxidation in the unsaturated zone has several potential advantages over that in the saturated zone: (1) the concentrations of O_3 that can be achieved in the gas phase are orders of magnitude higher than is obtained in aqueous solutions, (2) O_3 is more stable in the gas phase than water, (3) O_3 diffusive transport is much greater than in water, and (4) higher flow velocities can be achieved in the unsaturated zone than are possible in ground water (Masten and Davies, 1997). Additionally, the mass delivery of gaseous O_3 in the unsaturated zone is generally much greater and potentially more effective than in the saturated zone. However, delivery and transport of O_3 gas in the unsaturated zone is much more vulnerable to preferential pathways attributed to heterogeneities in permeability. Consequently, short circuiting of O_3 gas may prevent adequate delivery of O_3 to targeted zones. Spatial monitoring of O_3 in the unsaturated zone is required to accurately assess the areal distribution of O_3 and to make the appropriate adjustments in the injection design and in O_3 delivery. Although targeting contaminants in the unsaturated zone limits oxidative treatment to zones above the water table, temporary depression of the water table exposes additional porous media and contaminants that may be vulnerable to in-situ O_3 oxidation. Unsaturated zone remediation may primarily use ozone injection points in the unsaturated zone, but sparging points just below the water table would help deliver O_3 into the smear zone associated with the capillary fringe.

Dry $KMnO_4$ and various concentrations of $KMnO_4$ solutions have been applied to the surface soil in the unsaturated zone. For example, TCE-impacted soil was treated with solutions of $KMnO_4$ in one-foot lifts (Balba *et al.*, 2002). Two injection techniques, (1) low pressure injection of $KMnO_4$ into wells and (2) high pressure injection into nozzles, were used to deliver $KMnO_4$ into the unsaturated zone. More uniform and better distribution of the oxidant was observed with the high pressure delivery method (McKay and Berini, 2002). Nested, hanging wells were used to deliver $KMnO_4$ into the unsaturated zone, which eventually drained to the saturated zones (Viellenava *et al.*, 2002). High initial injection pressures were used in these wells to hydrofracture the porous media, which created more flow pathways and greater oxidant delivery.

III.C.2. Contaminant Characteristics

III.C.2.a. Phase

Organic contaminants may be present in the aqueous phase (dissolved in water), solid phase (adsorbed onto aquifer material or soil), and as a non-aqueous phase liquid (NAPL). Chemical oxidation of organic contaminants can occur in all three phases. Many variables and site-specific conditions play a role in terms of which phase of the contaminant is oxidized. When contaminants are oxidized in the aqueous phase, increased concentration gradients and enhanced mass transfer and oxidation of contaminants occur from both the solid phase (desorption) and from the NAPL phase (dissolution) into solution.

In addition to the background oxidant demand, the quantity of oxidant and number of oxidant applications needed is dependent on the phase of contaminant present (NAPLs > solid > aqueous) and the associated phase-dependent mass transfer and mass transport limitations (Figure 3). Assuming mobile NAPL is determined to be present at a site, NAPL removal is considered an important first step in the remediation process. Removal of NAPLs by other methods (such as thermal) can usually be accomplished more cost effectively than by chemical oxidation and can be conducted in a manner to minimize NAPL mobilization into undesired areas. Chemical oxidation would then be more appropriate to use on the immobilized NAPLs (residual saturation) that remain in the porous media.

Due to the heat and large quantities of $O_2(g)$ released during Fenton oxidation, fire, explosion hazards, and safety issues may become important if the NAPL is volatile and flammable, such as gasoline.

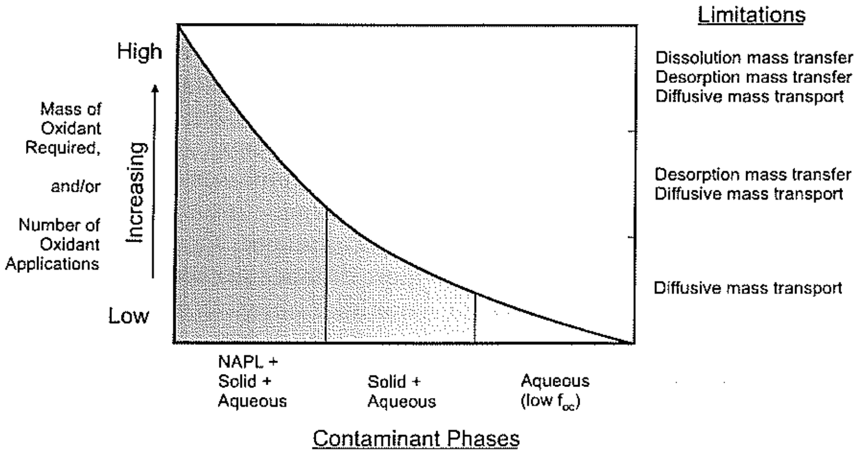


Figure 3. Impact of contaminant phases, mass transfer, and mass transport limitations on the mass of oxidant and/or the number of oxidant applications needed for ISCO. The presence of all three contaminant phases (NAPL, solid (adsorbed), aqueous (soluble)) represents the most challenging set of conditions, potential limitations, and mass of oxidant and/or number of oxidant applications.

III.C.2.b. Concentration

Chemical oxidation can be described by second-order reaction rate kinetics (Eqn 1). It is evident that the oxidant can react with either the target contaminant, scavengers (i.e., non-target reactants), and intermediates. The extent to which the oxidant reacts with either is dependent on the reaction rate constant of the reactant, and the concentration of the reactant. Therefore, the greater the concentration of contaminants relative to other potential reactants, the faster the reaction rate of the target contaminant. This partially explains why greater oxidation efficiency occurs in source zones where high concentrations of the target contaminants are present. The feasibility of treating relatively low dissolved concentrations of organic contaminants may not be as favorable, and these concentrations may be more effectively treated by other candidate technologies, such as monitored natural attenuation (MNA).

$$dO/dt = k_1 [O] [C] + k_2 [O] [S] + k_3 [O] [I] \qquad \textit{(Eqn 1)}$$

where:

k_1, k_2, k_3 = second order reaction rate constant (L/mol-s)
$[O]$ = concentration of oxidant ($\cdot OH$, MnO_4^-, O_3, $S_2O_8^{2-}$, $\cdot SO_4^-$) (mol/L)
$[C]$ = target contaminant (mol/L)
$[S]$ = scavenger (mol/L)
$[I]$ = intermediates (mol/L)

III.C.3. Subsurface Characteristics

Physical and chemical characteristics of the subsurface environment (hydrogeology, geology, geochemistry) vary from site to site and impact the fate and transport of the injected oxidant and reagents. Site characterization is critical to the feasibility assessment of ISCO and in the planning and design of pilot- and full-scale ISCO systems.

III.C.3.a. Geology

Fractures (cracks, fissures, joints, faults) are characterized by their length, orientation, location, density, aperture, and connectivity (Berkowitz, 2002). Transport of injected reagents into fractured media is generally much less predictable than into unconsolidated porous media, mainly due to the heterogeneity and uncertainty in fracture characteristics and the difficulty and expense in characterizing the fracture network. Tracer studies can be helpful to identify the interconnectedness between monitoring wells, the rate of ground-water transport, and the residence time of the injected water. Borehole hydrophysics can be used to assess ambient and stressed flow patterns and contaminant transport in fractured systems. These investigation methods provide general information on hydraulic characteristics and hydraulic control requirements of a tracer prior to oxidant injection. Due to density-driven transport of MnO_4^- and $S_2O_8^{2-}$ solutions, vertical transport may not be fully represented by a tracer study. Due to transport limitations of H_2O_2 and O_3 in fractured systems (i.e., within the matrix porosity, refer to Section III. C.1.a. Saturated Zone), Fenton and O_3 oxidation would have limited use in fractured systems.

Naturally occurring subsurface heterogeneities such as zones of high permeability (e.g., sand-filled paleochannel, fractures), as well as subsurface utility corridors and other anthropogenic subsurface disturbances, can act as preferential pathways. Preferential pathways found in fractured systems and unconsolidated porous media result in unpredictable flow patterns (rate, direction) for ground water and injected oxidant solutions. This can be a significant impediment to effective/uniform delivery of oxidant in the subsurface. Additionally, under high injection pressures, hydraulically-induced fractures of the media and/or "breakout" of the injected oxidant solution may occur. Both of these conditions result in disproportionate volumes of oxidant solution being injected over a small geologic interval. The lowest removal rates of TCE and DCE in ground water were found five feet from an O_3 injection point, compared to significantly higher removal rates in wells up to twenty feet away from the injection point (Masten and Davies, 1997). This example indicates that ozone sparged into ground water may be transported in specific and limited preferential gas channels that short-circuit and do not contact a significant portion of the region around a sparge point.

These problems can be detected and avoided early through good site characterization and ground-water monitoring. Also, shorter distances between injection wells minimizes the areal coverage and the oxidant transport distance per well, thus limiting the impact of these nonideal transport mechanisms.

III.C.3.b. Hydrogeology

The oxidants and reagents injected into the subsurface will undergo advective and diffusive transport. The transport distance is dependent on the method of delivery, persistence of the chemical, ground-water flow rate, density of the solution, and diffusive characteristics of the chemical and porous media (Figure 4). For example, slow reaction rate and long-term persistence of MnO_4^- in

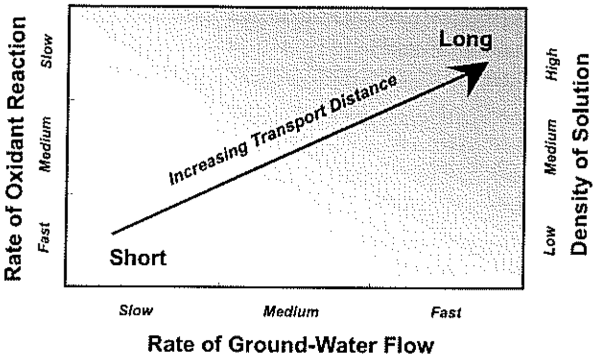


Figure 4. The transport distance through porous media of the injected oxidant is dependent on the rate of reaction of the oxidant, the rate of ground-water flow, and the density of the oxidant solution (density-driven transport).

aquifer materials has occurred under a variety of hydrogeologic environments including saturated sands, clays, sand-clay mixtures, alluvial materials, fractured shale, and fractured bedrock. Consequently, MnO_4^- can be transported longer distances than the other oxidants. The greater the hydraulic conductivity and hydraulic gradient of the aquifer, the farther the transport distance. Due to the fast reaction rate of O_3, H_2O_2, and some reagents (i.e., Fe(II), phosphate, acid), the ground-water flow rate and direction under most conditions will have a minimal impact on the post-injection oxidant transport. The vertical transport of the oxidant is affected by density of the oxidant solution and on vertical gradients (upward, downward) in the aquifer. The transport of MnO_4^- will be greatest when high concentrations are injected into an aquifer with high hydraulic gradient and conductivity. Under this set of conditions, MnO_4^- may migrate from the targeted zone and result in a lower oxidation efficiency (i.e., due to lower downgradient contaminant concentrations) or be transported into unintended locations (i.e., ground-water capture by pump and treat system). Downgradient drift is not always problematic since pinpoint resolution of source area boundaries is not commonly achieved and oxidation of downgradient contaminants may be needed. Similarly, long oxidant transport distances may be intentionally designed to target large, non-source area plumes.

III.C.3.c. Geochemistry

Permanganate oxidation is generally independent of pH in the range of 4 to 8 (Seigrist *et al.*, 2001) and thus will be effective over the pH range normally found in ground water. Acidic pH (pH 3 to 4) is optimal for Fenton-driven oxidation of organic contaminants. The buffer capacity in most aquifers represents significant acid-neutralizing capacity and maintains the ground-water pH near neutral, i.e., resistant to pH modification. Acidification of the target zone is often temporary and restricted to a zone near the injection well. In poorly buffered systems, acid transport and pH modifications may be easier to accomplish. Under naturally acidic conditions, pH modification may not be necessary. For example, high concentrations of Fe^{+2} and acidic conditions (pH 2 to 3) were measured at a site where large quantities of organic carbon were introduced into the ground water (i.e., the aquifer underlying former sludge drying beds) (U.S. DoD, 1999; Maughon *et al.*, 2000).

Reduced geochemical conditions favor the presence of reduced divalent transition metal ions such as Fe or Mn. Under this condition, the Fe^{+2} contributes to the Fenton reaction, and both Fe^{+2} and Mn^{+2} contribute to the activation of the $\cdot SO_4^-$. For example, significant chlorinated VOC reduction was achieved using persulfate in a glauconitic (iron-rich) sand containing 3 to 15 mg/L Fe^{+2} (Sperry *et al.*, 2002). Reduced geochemical environments are also a source of treatment inefficiency due to the abundance of reduced chemical species that consume oxidant and/or scavenge radicals. Natural organic carbon present in soil and aquifer material can play an important role in oxidative reactions (refer to Section III.F.4.b. Natural Organic Matter).

III.D. Site Requirements and Operational Issues

III.D.1. Site Characterization Data

An effective delivery of the oxidant to the targeted zone(s) is a critical element to achieve success with ISCO. Therefore, an important ISCO design criteria is to identify the location(s) of the contaminant(s) in the subsurface. Site characterization data is required to identify the type(s), distribution, and phase/concentration of the contaminants (Table 11). This information is used in the planning and the design of the oxidant injection program (i.e., dosage, injection locations, and rates).

Site characterization and ISCO efforts are often focused in source areas where NAPL may be present. Removal of mobile NAPL, if present and practical, is important since NAPLs could be mobilized during ISCO. Assuming the NAPL (LNAPL, DNAPL) can be located, removal would probably be more cost efficient using other technologies than through ISCO. A significant improvement in the development in site characterization techniques and technologies to locate and delineate suspected DNAPL source

Table 11. Site Characterization Data Needed for ISCO

Parameter	Purpose of the Data/Information
Target Contaminant	
Type(s)	To select which oxidant is most suitable for the specific contaminant(s).
Distribution	To determine where to deliver the oxidant (spatial delivery of the oxidant).
Phase/concentration	Aqueous/sorbed/NAPL — to identify potential hot spot areas where multiple applications will be required; to estimate contaminant mass which may be used to estimate the total oxidant mass required (see Section III.C.2).
Geology and Hydrogeology	Estimate rate of oxidant injection based on aquifer hydraulic properties. Information on hydraulic conductivity and gradient and aquifer heterogeneities can be used to identify post-injection flow direction and rates. Assess whether nearby receptors could be impacted (see Section III.C.3).
Aquifer Material/Soil/ Ground Water	Analyzed for organics to quantify and delineate contaminant distribution; used for bench-scale feasibility testing (contaminant oxidation, oxidant demand testing); analyzed for metals to identify hot spot or problematic conditions where pH- or redox-sensitive metals may become mobilized during ISCO.
pH, Buffer Capacity	To assess whether pH modification is needed; acidic pH (3 to 5) is optimal for Fenton oxidation; pH modification will be difficult to achieve in highly buffered soil/aquifer materials; carbonate and bicarbonate buffer species act as radical scavengers in Fenton and persulfate oxidation.
E_h (electrode potential)	General indicator of oxidant demand.
Reduced Inorganics	Soluble metals (Fe(II), Mn(II)), sulfides indicate reducing conditions.

zones has occurred in recent years. The cost and level of accuracy achievable by source zone characterization tools can only be answered on a site-specific basis (U.S. EPA, 2001). In practice, delineating DNAPL source zones and providing an accurate estimate of the mass and spatial distribution of the DNAPL can be challenging due to the heterogeneous distribution of the DNAPL. Extensive sampling and analysis of ground water and aquifer material is usually required to obtain a reasonable estimate of contaminant distribution. Oxidant dosage requirements have been estimated by some practitioners based on the mass of contaminant(s), in conjunction with oxidation stoichiometry and the natural oxidant demand. Other methods are also used to estimate the total oxidant required that are not based on contaminant mass estimates (refer to Section III.E.2. General Conceptual Approach to ISCO).

Geologic (lithology, stratigraphy, heterogeneities) and hydrogeologic (hydraulic conductivity, gradient, porosity) characterization will assist in development of a conceptual model used to assess the fate and transport of the contaminant(s), injected oxidant, and reaction byproducts. This information can be used, in conjunction with the contaminant data, to select the location and vertical intervals for oxidant injection and to assess oxidant transport. Important parameters that can be easily overlooked are man-made and naturally occurring preferential pathways. Subsurface utilities and high hydraulic conductivity flow paths may result in the disproportionate transport of oxidant, heat, and gas, and unanticipated exposure pathways. Even well-characterized sites are likely to have heterogeneities that are difficult to quantify, yet play an important role in ISCO. Pilot-scale studies are useful because they provide an opportunity to acquire localized fate and transport data for the injected oxidant and to refine performance monitoring efforts. Aquifer material, soil, and/or ground-water samples are collected for site characterization (organic contaminants), bench-scale feasibility testing, and analysis for general parameters. In some cases, high background concentrations of metals, or co-disposal of metals and organics, represent conditions that are conducive for metals mobilization during ISCO.

Due to the uncertainties in site characterization, estimating contaminant mass, oxidant delivery, etc., the need for multiple oxidant injections in the targeted zone cannot be overemphasized.

III.D.2. Required Site Infrastructure

Infrastructure requirements for permanganate, peroxide, and persulfate include a water supply, for dissolution and/or dilution of the reagent. Extraction wells and above-ground treatment are necessary if oxidant recirculation (injection, recovery, re-injection) is used. A disposal option for treated/untreated water may also be required. An open, unobstructed area is necessary to accommodate the oxidant mixing apparatus, batch storage tanks, piping, etc. An electrical power supply or generator will be required for pumping and pressure injection of the oxidant solutions. Direct push injection technologies are rig-mounted and site access for large or small vehicles in the injection area is a consideration.

The small radius of influence of the Fenton's reagent (H_2O_2, Fe^{+2}) requires closely-spaced injection points that involve an open area clear of underground utilities. Due to the heat, $O_2(g)$, and possible volatile emissions that could be released, access should be restricted to the injection area. Very high temperatures often result from Fenton oxidation and have melted polyvinylchloride (PVC) plastic pipes (the crystalline melt temperature of PVC is approximately 200 °C). Injection wells should be constructed with stainless or carbon steel. A soil vapor extraction system in conjunction with an impervious cover and off-gas treatment may be necessary to capture volatile emissions from the injection area. Excessive pressure build-up may result in dangerous gas/steam venting conduits at the ground surface (randomly distributed) and buckling/heaving of asphalt parking lots (mostly under high H_2O_2 concentrations).

In-situ ozonation requires an on-site ozone generator, gas handling and distribution equipment, and injection wells. Extraction wells (i.e., a soil vapor extraction system) may be necessary to control O_3 flow directions (Masten and Davies, 1997). Subsurface heating and the associated remedial technology infrastructure would be needed for thermal activation of persulfate. Radio frequency heating, electrical resistance heating, or any other thermal technology, is technically feasible for heating the subsurface (Liang *et al.*, 2001; 2003).

III.D.3. Regulatory Constraints on Injection of Reagents

Regulatory permitting requirements for oxidant injection have been compiled and organized by state (ITRC, 2005). The injection of oxidants and reagents are regulated primarily through the Underground Injection Control (UIC) program of the Safe Drinking Water Act (SDWA), the Resource Conservation and Recovery Act (RCRA), the Comprehensive Emergency Response, Compensation, and Liability Act (CERCLA), and the Emergency Planning and Community Right to Know Act (EPCRA). Through these environmental programs, regulatory approval is required and an oxidant injection permit may also be required from some state environmental agencies. Some states have issued variances and permit exceptions that may affect ISCO activities. Regulatory examples of six states (NJ, CA, FL, KS, MO, TX) are provided in which chemical oxidation can be used for soil and ground-water remediation (ITRC, 2005). Individual states may have more restrictive regulations than the Federal programs listed above. Regulatory constraints on each ISCO project should be assessed on a case-by-case basis.

EPA's secondary maximum contaminant level (SMCL) for manganese in water (0.05 mg/L) is a secondary drinking water standard due to aesthetics (taste, color, staining) (Table 12) (U.S. EPA, 1992). The post-oxidation manganese content of aquifer material can be high. At one site where $KMnO_4$-driven ISCO was used, post-oxidation ground-water concentrations one year later exceeded the EPA SMCL for Mn (Crimi and Siegrist, 2003). Ideally, due to the insolubility of Mn as $MnO_2(s)$, ground-water concentrations of Mn will be minimal under most conditions.

Human consumption of MnO_4^- by recovery in water supply wells represents a potential exposure pathway and a serious health threat (but has not been reported). The characteristic purple color of MnO_4^-, or pink color at low concentration, could alert water treatment plant operators and potential consumers of the oxidant-tainted water. Releases to nearby surface waters could have serious environmental impact on biota and should be prevented.

Technical grade $KMnO_4$ may contain impurities, including Cr and As. Due to the low maximum contaminant level (MCL) in drinking water set by EPA for these metals (0.1 mg/L total Cr MCL; 0.01 mg/L As MCL) (U.S. EPA, 2002), injection of technical grade $KMnO_4$ may result in exceeding the MCL for these elements in the injection zone. Although the attenuation of these metals has typically been achieved within acceptable transport distances and time frames (see Section II.C.1.f., Metals Mobilization/Immobilization), a site-specific assessment should be conducted to determine whether these parameters need to be monitored. $KMnO_4$ is produced by some manufacturers specifically to lower the concentrations of these impurities (at additional cost). Additionally, low concentrations of the oxidant solution can be used to minimize metals concentration in the ground water. $KMnO_4$ will exhibit minute amounts of radioactivity. Radioactive potassium-40 (^{40}K) is a small fraction (about 0.012%) of naturally occurring potassium and is primarily beta-emitting, but also involves gamma radiation (ANL, 2002). This may become an issue at radionuclide contamination sites, such as some DOE sites, where it is important to monitor and limit radioactivity.

ISFO may also involve the injection of acid(s), iron catalyst, and/or stabilizers, any of which may be subject to regulatory constraints. Regulators may also be concerned about the possibility of contaminant volatilization and subsequent releases to the unsaturated zone, basements, and air. Similarly, releases of both volatile organics and O_3 during in-situ ozonation are a regulatory concern. The use of a conservative insoluble tracer gas (e.g., helium (He)) during air sparging/injection and/or O_3 sparging/injection could provide fate and transport information of volatile organics, O_3, and the proper placement of soil vapor monitoring points. Sulfate is a reaction byproduct from in-situ persulfate oxidation. Since persulfate is injected at high concentration, and can persist for weeks to months, the potential for persulfate and/or sulfate to migrate to nearby receptors should be assessed. Although there are well-documented biotic and abiotic attenuation mechanisms, ground-water monitoring is recommended. EPA has established a secondary MCL for sulfate in water (250 mg/L) due to a salty taste (Table 12).

III.E. Field-Scale Implementation and Engineering Design Considerations

III.E.1. Treatment Objectives

The treatment objectives for ISCO vary from site to site and include, but are not limited to the following: reduction in contaminant toxicity/mass/concentration (risk based or maximum concentration levels (MCLs)), and/or a reduction in contaminant mass flux across a site boundary. ISCO is a source depletion technology that is capable of removing substantial amounts of DNAPL in source zones at sites with favorable hydrogeologic conditions (i.e., less heterogeneous and more permeable subsurface conditions); however, achievement of drinking water MCLs in these source zones as well as source zones in more challenging heterogeneous hydrogeologic conditions (e.g., bedrock, karst systems, multiple stratigraphic units) is unlikely (U.S. EPA, 2001). However, ISCO is capable of achieving partial DNAPL depletion, which may provide other performance benefits including eliminating the mobility of the DNAPL, and reduction in the mass discharge rate of DNAPL constituents from the source zone, which may reduce environmental risks and life cycle costs (U.S. EPA, 2001). One of the alternative metrics for judging the performance of source-mass depletion technologies is contaminant mass discharge, defined as the summation at a point in time of point values of contaminant mass flux across a vertical control plane encompassing the plume and perpendicular to the mean ground-water flow direction at a location downgradient of the DNAPL source zone. Theoretical analysis and field data indicate that partial DNAPL mass depletion in the source zone reduces contaminant mass discharge (U.S. EPA, 2001).

ISCO is often deployed in source areas to minimize long-term sources of ground-water contamination. However, ISCO has also been deployed at property boundaries for the purpose of preventing off-site migration of ground-water contaminants, and in weathered plumes where NAPL is present in small volumes, or absent altogether. In this scenario, the majority of the contaminants are present as soluble and sorbed phases at lower concentrations (than in source zones). Under these operating conditions, ISCO has a much higher probability of achieving

Table 12. EPA Secondary Maximum Contaminant Levels (SMCL) (Abbreviated List)

Contaminant	Secondary MCL*	Noticeable Effects Above the SMCL
Iron	0.3 mg/L	Rusty color; sediment; metallic taste; reddish or orange staining
Manganese	0.05 mg/L	Black to brown color; black staining; bitter metallic taste
Sulfate	250 mg/L	Salty taste

* mg/L is milligrams of substance per liter of water
http://www.epa.gov/safewater/consumer/2ndstandards.html

the MCL objective, than in source zones that contain NAPLs. ISCO has also been used to (1) reduce the mass flux to pump and treat systems, and (2) to reduce the concentration gradient across a low-permeability barrier in hydraulic containment systems.

Due to significant challenges required of ISCO to meet stringent clean-up standards, such as MCLs in source zones, monitored natural attenuation is an integral component in the overall remedial strategy for source zone and downgradient plume.

III.E.2. General Conceptual Approach to ISCO

It is uncertain how bench-scale oxidant demand values relate quantitatively to the actual oxidant demand measured under field conditions. It should be recognized that conditions at bench-scale (e.g., solids:solution ratio, mixing, contact between oxidant/reagents and contaminants/aquifer material, etc.) are significantly different than field-scale, and that samples used in the bench-scale study may not fully represent field conditions (i.e., heterogeneities). Correspondingly, there is uncertainty in data interpretation and how the information is used in pilot- and field-scale applications. Review of numerous ISCO reports reveals that different approaches are used to design oxidant (MnO_4^-, H_2O_2) loading for pilot- and full-scale ISCO systems. However, economic and infrastructure resources/limitations also play a strong influence in the oxidant dosage and injection program.

A single, well-documented, and well-demonstrated oxidant loading and delivery design approach has not been established for any oxidant. Overall, the state of the science of ISCO involves the combined use of best engineering and scientific judgment (site characterization, feasibility study testing, remedial design, etc.) in conjunction with trial and error. Due to the inherent uncertainty with contaminant distribution, subsurface heterogeneities, and mass transfer/transport mechanisms that occurs at most sites, ISCO requires multiple iterations between oxidant application and performance monitoring. Through this process, clean areas can be identified that require no further treatment, and hot spot zones can be identified which permits the strategic delivery of additional oxidant to accomplish the treatment objectives.

III.E.2.a. Permanganate Oxidation

There are two general approaches used with MnO_4^-: the "high oxidant loading" and the "iterative oxidant loading" approaches. Some approaches reported in the literature use various combinations of the two methods described below.

III.E.2.a (1) High Oxidant Loading

The "high oxidant loading" approach seeks to apply all necessary oxidant mass in one initial application. This approach utilizes oxidant demand results and information from bench- and pilot-scale oxidation testing in conjunction with empirical factors to estimate the oxidant loading for an equivalent mass of contaminated aquifer material at field-scale in the targeted zone(s). Empirical factors used in the calculation have been based on a margin of safety, field experience, types of aquifer materials, oxidation stoichiometry, estimated mass of contaminant(s), reaction rate kinetics, differences between short-term and long-term oxidant demand tests, etc. Subsequently the oxidant load is estimated and delivered into the targeted zone(s). It is assumed that the aquifer samples used in the bench test are representative of the targeted zone(s). This approach may potentially result in fewer iterations between oxidant injection and ground-water monitoring, fewer field mobilizations, and potentially lower cost. Due to heterogeneous contaminant distribution, variability in background oxidant demand, and the inability to uniformly deliver the oxidant, this approach may result in higher oxidant loading (and cost) than needed. Higher oxidant loading/concentration may result in the transport of oxidant from the targeted zone, higher oxidant demand, greater metals mobilization, greater Mn residual, and may eventually require the same number of iterations and mobilizations as in the iterative oxidant loading approach.

III.E.2.a (2) Iterative Oxidant Loading

This approach recognizes that multiple iterations between oxidant injection and post-oxidation monitoring will be required. Results and information from site-specific bench-scale oxidation testing may or may not be used. It is assumed that aquifer samples in bench-scale studies may not be representative of the target zone; contaminant distribution is heterogeneous; moderate oxidant loading may permanently reduce contaminant concentrations over large areas of the target zones; contaminant concentrations may be reduced and treatment objectives achieved without satisfying the total oxidant demand of the aquifer material; and subsequent, perhaps heavy, oxidant loading(s) may be required in smaller hot-spot zones where mass transfer and mass transport limitations exist. The advantage of this approach is that potentially lower total oxidant loading and costs may occur. The disadvantage is that potentially a greater number of iterations between monitoring and oxidant injections will occur which could increase cost.

III.E.2.b. Fenton Oxidation

A well-documented and demonstrated oxidant loading and delivery design approach has not been established and published. Several factors strongly influence the mass of H_2O_2 required. Some ISFO vendors base the mass of H_2O_2 to be delivered on an estimate of the mass of contaminants, reaction stoichiometry, and empirical factors. Empirical factors used in these calculations have been based on a margin of safety, field experience, and types of aquifer materials. An estimate of the mass of contaminants in conjunction with reaction stoichiometry provides an initial theoretical estimate of the H_2O_2 demand under ideal conditions. However, due to the difficulty in accurately estimating the mass of contaminants in the subsurface, this approach should be considered a very rough approximation of the minimum amount of H_2O_2 required. Additionally, other factors and nonideal mass transfer and mass transport conditions in the subsurface must also be considered. H_2O_2 reactions that do not produce radicals (nonproductive reactions) and reactions that occur between radicals and non-target species (scavenging) lower the oxidation efficiency. H_2O_2 and ·OH depletion in these reactions results in greater quantities of H_2O_2 required for ISFO.

Once hydroxyl radicals are formed, they are transported only a few nanometers due to their high reactivity. Therefore, a fundamental tenet of ISFO is that the H_2O_2, Fe(II), and contaminant should be in the same location at the same time for oxidation to occur. The fast reaction rate of H_2O_2 represents a significant limitation in its delivery. Very simply, the rate of H_2O_2 transport must be greater than the reaction rate. Numerous cases have been reported where H_2O_2 delivery was restricted to locations near the injection wells/points (i.e., within a few feet), which was attributed to rapid H_2O_2 reaction rates.

An analytical solution was used to simulate H_2O_2 transport in porous media for steady-state, radial flow in homogeneous porous media with pseudo first-order degradation of H_2O_2 (Figure 5). In this theoretical analysis, the same volume and concentration of H_2O_2 solution were injected at different rates. A low H_2O_2 injection rate limited H_2O_2 distribution and increasing the injection rate resulted in increasing the transport distance and lowering the injection time.

Acidification of the injected oxidant solution will reduce the reaction rate of H_2O_2. Fast delivery of the H_2O_2 solution at lower pH will increase the transport distance of H_2O_2 into the aquifer. Potential limitations of high injection rates may involve either low hydraulic conductivity or excessive injection pressure. Shorter injection well spacing will reduce the lateral H_2O_2 transport distance required per well and is an additional design parameter that could be used to increase H_2O_2 coverage in the targeted zones.

III.E.2.c. Ozone Oxidation

Few details are available that describe the steps and criteria used in estimating the mass of O_3 needed for in-situ ozonation. One estimate of the average stoichiometric demand

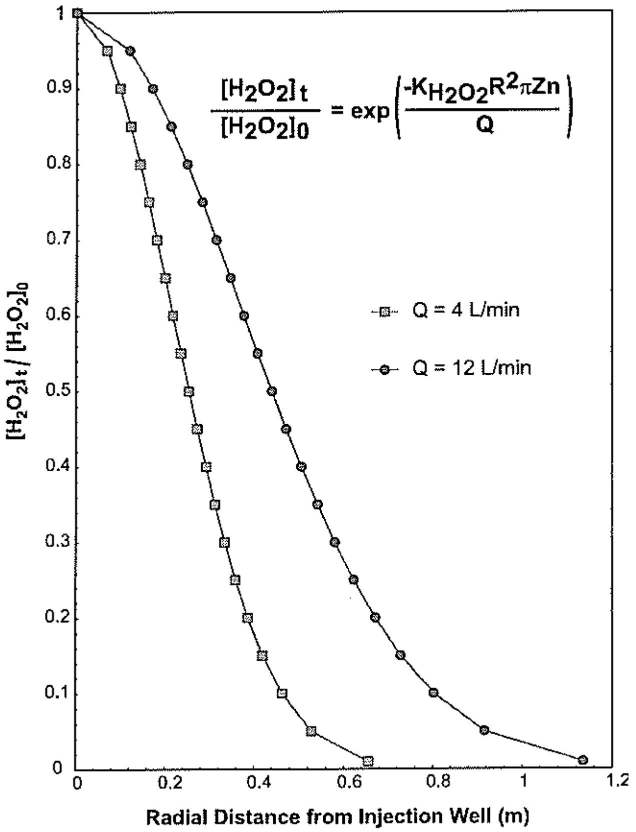


Figure 5. H_2O_2 undergoes reactive transport in porous media. The relative concentration of H_2O_2 is illustrated for two oxidant injection rate conditions (4 L/min and 12 L/min; steady-state, radial flow, pseudo first-order degradation kinetics; same volume (30,000 L) and concentration of H_2O_2 solution injected). The faster the injection rate, the greater the transport (radial) distance of H_2O_2. The equation was solved for radial distance (R). Units were converted for dimensionless terms ($[H_2O_2]_t$, $[H_2O_2]_0$ = time dependent and initial H_2O_2 concentration, respectively; $K_{H_2O_2}$ = H_2O_2 degradation rate (0.91 hr^{-1}); R = Radial distance (m); Z = Vertical interval (3 m); n = Porosity (0.3); Q = Flow rate (L/min)).

for phenanthrene was 8.69 g ozone per g phenanthrene (Kim and Choi, 2002). The ratio of ozone mass to PAH hydrocarbon mass at a former fuel oil distribution terminal was 7.6:1 (Wheeler *et al.*, 2002). An ozone dosage of about 0.5 g ozone/kg soil resulted in the removal of 81% of 100 mg/kg pyrene (Masten and Davies, 1997). These preliminary bench-scale results, in conjunction with estimates of the contaminant mass, could provide a general indication of the mass of O_3 required. However, under field conditions, nonideal mass transfer and mass transport mechanisms, reactive transport, and reactions between non-target species and O_3 not represented in the bench-scale studies will result in a greater O_3 demand. Remediation of a former manufactured gas plant site used a total 52 lbs O_3/day of 5 to 10% O_3 and 90 to 95% O_2, injected at 7.5 scfm and 20 psi, with occasional increases to 8 to 12% O_3 for contaminant hot spots (Cambridge and Jensen, 1999). The O_3 concentration in the gas stream, the gas flow rate, and the injection pressures should be included when specifying the O_3 mass delivery rate.

O_3 will react with OH^- in water, which continuously results in an O_3 demand, suggesting that the O_3 demand is essentially infinite. This is similar to Fenton oxidation where H_2O_2 reaction is infinite. Therefore, in-situ O_3 oxidation involves a trial and error approach where O_3 is delivered and ground-water monitoring is used to assess the extent of O_3 transport and distribution and contaminant destruction. Modifications to the O_3 injection strategy to enhance O_3 coverage and/or transport include closer injection well spacing, and/or faster O_3 mass delivery rate (increasing O_3 content, gas flow rate, or O_3 pressure).

III.E.2.d. Persulfate Oxidation

There are similarities between persulfate and permanganate oxidation (see Section III.E.2.a, above). For example, the oxidant demand measured in bench-scale studies, in conjunction with empirical factors, has been used to estimate the oxidant loading for an equivalent mass of contaminated aquifer material at field-scale. A similar approach could possibly be used with persulfate. However, few details are available that describe the steps and criteria used in estimating the mass of $Na_2S_2O_8$ to inject, the persistence of $Na_2S_2O_8$, and the development of oxidant injection guidelines. Some information about application rates and loading approaches can be gleaned. The sequential use of $Na_2S_2O_8$ and MnO_4^- in a pilot-scale field test was conducted involving an aquifer contaminated with residual TCE DNAPL (Droste *et al.*, 2002). It was proposed that $Na_2S_2O_8$ would satisfy the majority of the natural oxidant demand, thus reducing the MnO_4^- demand. Two treatment zones (each about 8000 m^3) were treated with a total of 8200 kg $Na_2S_2O_8$ in 4,300,000 L water (1.9 g/L solution) in a 64-day long injection period. Assuming uniform distribution of $Na_2S_2O_8$, a soil bulk density of 1.7 g/cm^3, and a porosity of 0.36, the $Na_2S_2O_8$ loading rate was approximately 0.3 g $Na_2S_2O_8$/kg soil. The $Na_2S_2O_8$ application was soon followed by permanganate injection, indicating that the iterative oxidant loading approach was not conducted in this test, at least not for $Na_2S_2O_8$.

The sequential use of $Na_2S_2O_8$ and MnO_4^- at pilot-scale was conducted to assess the efficacy of each oxidant for the destruction of CVOCs (e.g., TCE, DCE, and VC) (Sperry *et al.*, 2002). A mixture of 645 kg $Na_2S_2O_8$ and ground water/potable water (40 g/L) was injected into a 340 m^3 test zone into three wells (2.5 to 3.0 L/min per well) for 4 days at 8 hrs/day. Assuming uniform distribution of $Na_2S_2O_8$, a soil bulk density of 1.7 g/cm^3, and a porosity of 0.36, the $Na_2S_2O_8$ loading rate was approximately 1.1 g $Na_2S_2O_8$/kg soil. Again, the $Na_2S_2O_8$ injection was immediately followed by injection of $KMnO_4$ indicating that the iterative oxidant loading approach was not conducted in this test, at least not for $Na_2S_2O_8$.

The $Na_2S_2O_8$/kg loading rate was 0.3 g $Na_2S_2O_8$/kg soil in the test where the oxidant was intended to satisfy the natural oxidant demand, and 1.1 g $Na_2S_2O_8$/kg soil in the test where the oxidant was intended to treat the contaminants. The $Na_2S_2O_8$ concentration varied widely in these two tests (1.9, 40 g/L) indicating that a "high oxidant loading" approach over smaller areas is a design option, and may have been intended to significantly decrease the contaminant mass in just one application.

III.E.3. Oxidant Delivery

The minimum volume of H_2O_2 injected should be sufficient for full coverage (saturation; pore volume injection) of the targeted zone. Multiple pore volumes of H_2O_2 may be required. Simple calculations can be used to provide a quick check on this important design criteria but it is often overlooked. Similarly, full coverage of the target area is required in O_3 oxidation involving either dissolved O_3 (O_3(aq)), O_3 sparging, or O_3(g) injection in the unsaturated zone. Due to the high concentrations of MnO_4^- and $S_2O_8^{2-}$ and subsequent density-driven transport (and diffusive transport), full coverage of the targeted zone may be achieved without injection of one pore volume.

Injection of any oxidant solution into a source area can result in the displacement of contaminated ground water from the source area and transport into potentially uncontaminated areas. An outside-in delivery design could minimize the impact from the lateral displacement of contaminated ground-water. Other site-specific strategies could be developed to prevent the spread of contaminated ground water during ISCO. Similar delivery methods are used for both permanganate and persulfate. Although persulfate oxidation is an emerging technology, the following discussion is also applicable to the delivery of persulfate into the subsurface.

MnO_4^- delivery techniques include direct push technology, injection wells (with or without recirculation), injection and recovery (push-pull in wells), hydrofracturing, and application/infiltration at the ground surface. Direct push technology (GeoProbe, lance permeation, etc.) provides wide flexibility both in the location and the vertical interval for oxidant injection. Ideally, oxidant injection (1 to 2 gpm, 20 to 30 psi) occurs in short (approximately 0.5 to 2 ft) screened intervals resulting in the delivery of a thin layer of oxidant solution into the aquifer (Figure 6). This injection strategy minimizes the lateral displacement of contaminated ground water in the injection zone. The oxidant is injected at 5- to 10-ft intervals over the depth of the targeted zone and density-driven and diffusive transport of the oxidant between the vertical injection layers results in interlayer distribution of the oxidant solution. Nonideal transport of the oxidant due to heterogeneities can result in various patterns of oxidant distribution and the actual distribution should be confirmed with a good monitoring system. Oxidant leakage at the ground surface and breakout into non-targeted zones can result from excessive injection pressures. Injectors and wells should be sealed to prevent short-circuiting. Injection locations are sometimes backfilled with a cement/bentonite material immediately after the direct push tool is extracted to minimize short circuiting of contaminants. Subsequent injection of oxidant in between previous injection points and at different vertical intervals allows flexibility in oxidant distribution. The direct push technology may not be possible in some geologic environments where rocks/cobbles/boulders prevent the tool from advancing into the subsurface.

Injection wells can be constructed with a wide range of materials (PVC, stainless steel, etc.). Wells can be used

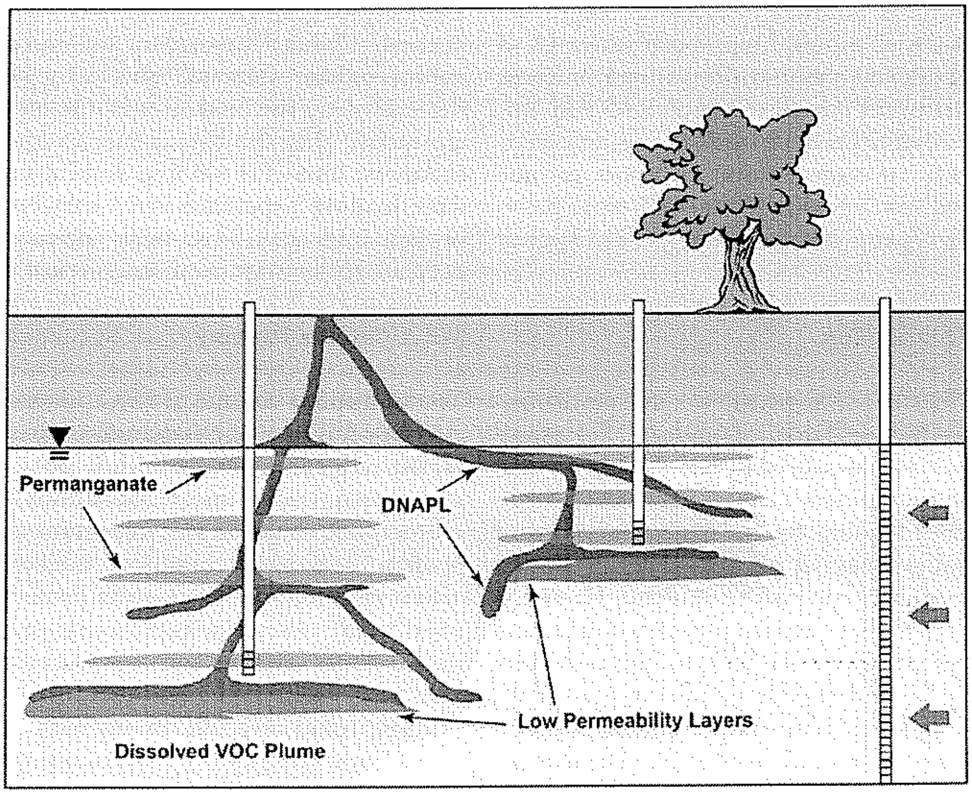


Figure 6. In-situ permanganate oxidation involving the emplacement method of oxidant delivery. Direct push technology can be used to inject the permanganate solution over short-screened intervals. Delivery of the oxidant over short-screened intervals can reduce the displacement of contaminated ground water relative to injection over longer-screened intervals. Stacked, intermittent layers (5 to 15 ft) of oxidant will disperse vertically and laterally with time.

to re-inject oxidant solutions but re-injection is restricted to the same physical location. The vertical interval for oxidant injection can be varied either by using nested wells or by the use of packers to utilize specific screened intervals. Oxidant injection at high pressures in nested or packed wells may result in hydraulic short-circuiting into the adjacent nested wells above and/or below the well where oxidant is injected. Additionally, excessive injection pressures should also be avoided to minimize oxidant breakout into non-targeted zones via hydraulic fracturing of the porous media. Ground-water pumping in adjacent wells (until breakthrough of the oxidant occurs) may be used to control/enhance the directional transport of the oxidant. Oxidant recirculation between injection and recovery wells is occasionally used to enhance delivery/distribution (Figure 7). This injection method is usually deployed in low-permeability materials to enhance the delivery of the oxidant. Recirculation can involve significant additional expenses to pump and treat the ground water before it is re-injected. Expenses with recirculation systems include but are not limited to engineering, air stripping, filtering of solids (MnO_2(s), silicates, etc.), re-amendment with $KMnO_4$/$NaMnO_4$, disposal of excess water, piping, tanks, electricity, etc.

Oxidant flooding of former surface impoundments (or topographical depressions) with underlying contaminants can be used to deliver MnO_4^- solutions over large areas. Subsequently, infiltration of the oxidant solution into the contaminated sediments can result in effective delivery and oxidative treatment. The infiltration surface should be well-graded to allow uniform distribution of the oxidant solution over the ground surface, and to prevent accumulation and infiltration of the oxidant solution over smaller areas. Large diameter (8-ft) augering was used to deliver $KMnO_4$ to 47 ft below grade into the unsaturated and saturated zones (Gardner *et al.*, 1998). Horizontal wells in either the saturated or unsaturated zone may also provide an effective delivery technique. Emplacement of $KMnO_4$ into fractured silty clay soils to treat TCE was investigated (Siegrist *et al.*, 1999). Laboratory experiments and modeling were used to investigate the feasibility of emplacing solid $KMnO_4$ into vertical wells. Ideally,

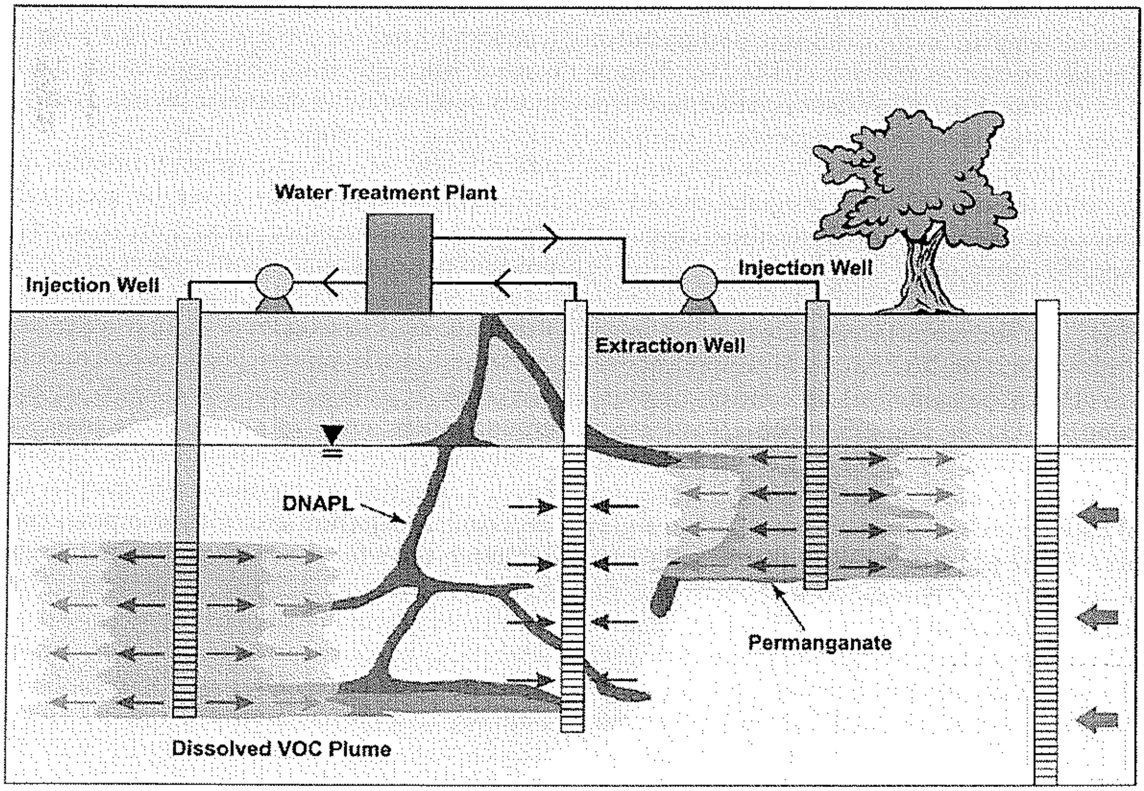


Figure 7. In-situ permanganate oxidation involving the recirculation method. Injection and extraction wells are used to deliver and recover the oxidant solution. Above-ground treatment is required to remove particulate matter (i.e., MnO_2(s), sand, silicates) and possibly COCs/ VOCs, and to re-amend the ground water with permanganate before re-injection.

the MnO_4^- would slowly diffuse into the ground water and form a treatment zone to treat contaminant plumes (Li and Schwartz, 2004b).

H_2O_2 injection requires injection wells that can withstand elevated pressures and temperature. Exothermic reactions and elevated temperatures that result during ISFO weakens PVC material and the elevated pressure causes material failure. Consequently, wells should not be constructed of PVC under these conditions (refer to Section II.C.2.e. O_2(g) Generation and Exothermic Reaction). Injection wells constructed of stainless or carbon steel have been used successfully under these conditions. Injection wells should be sealed to prevent hydraulic short-circuiting along the well bore and the potential release of H_2O_2 solution at the ground surface. During H_2O_2 injection, O_2(g) expansion, elevated pressure, and breakout of H_2O_2 can occur. This can occur more easily when injecting at shallow intervals. Breakout could expose site workers to high concentrations of H_2O_2, acid, high temperature liquids and/or steam, and contaminants. Careful monitoring should be performed during injection to detect this condition and trigger cessation of injection activities. Due to the rapid reaction of H_2O_2, closely spaced injection wells and fast injection rates are required for the oxidant to be distributed into the aquifer (refer to Section III.E.2.b. Fenton Oxidation). In-situ Fenton oxidation often involves vendor-specific reagent mixes, injection methods, equipment, pressures, and strategies. A critical review of the oxidant and reagent injection program should be conducted to assure adequate delivery of these chemicals under site-specific conditions.

Delivery of O_3 into the subsurface mainly involves injection wells (refer to Section II.C.3.b. In-Situ Application). Extraction wells may be useful to help control the transport direction of O_3 in the subsurface (Masten and Davies, 1997). Horizontal wells have been used to introduce O_3 into the saturated zone (Nelson and Brown, 1994), and may be useful in combination with sparging technologies. However, it is not clear that the potential advantages of installing horizontal wells warrants the additional costs (Masten and Davies, 1997). O_3 remediation at a former manufactured gas plant site used both vertical injection wells in the saturated zone as ozone sparge points and a horizontal well 6 ft under the water table that had a 135-ft screened section (Cambridge and Jensen, 1999). Injection strategies could include an initial phase of operation consisting of sparging with air while collecting the vapors with a soil venting system, such as at a PCE-contaminated ground-water site in Carson City, NV (Masten and Davies, 1997).

III.E.4. Monitoring

III.E.4.a. Ground-Water Monitoring

Ground-water contaminant concentrations represent an integrated measure of the type, phase, and magnitude of contaminants in the subsurface. Therefore, the ground water can generally be used as a reliable indicator of treatment performance, as a diagnostic tool to design and direct oxidant applications, and to determine optimal oxidant delivery location(s). For example, a reduction in the concentration of organic contaminants between pre- and post-oxidation, or simply whether the resulting concentrations approach established cleanup levels are often used as metrics for performance evaluation. Additionally, persistence of VOCs indicates a source area that requires additional oxidant application. Fortunately, oxidants, especially $KMnO_4$ and $Na_2S_2O_8$, can be distributed in source areas in a manner that does not require pinpoint accuracy of contaminant mass and location. Several mass transfer and mass transport limitations present significant challenges to effective and efficient ISCO. These include slow oxidant transport through low-permeability layers, preferential oxidant transport through high hydraulic conductivity zones (inability to deliver the oxidant to the target area), fast oxidant reaction rates, background oxidant demand, excessive demand in hot spot areas, etc. These conditions, and others, will ultimately limit ISCO. The extent to which each of these potential limitations manifest themselves at a site may never be accurately assessed. However, the combined effect can be assessed through pre- and post-oxidation ground-water monitoring.

Rebound in post-oxidation ground-water contaminant concentrations is time dependent and involves (1) the mass transfer from adsorbed and DNAPL phases into the ground water, and (2) contaminant mass transport in ground water to wells where it can be sampled and analyzed. Collection of ground-water samples immediately after oxidant injection and/or consumption does not allow sufficient time for rebound and would likely represent transient (nonequilibrium) conditions. Ground-water monitoring should be delayed for these processes to occur after ISCO has been implemented. Site-specific contaminant transport calculations can be used to estimate the time required for contaminant transport to monitoring well locations after oxidant consumption. Estimates of the duration of rebound are not well-documented and may easily require months to fully rebound. In Fenton and O_3 oxidation, O_2(g) in the porous media may interfere with mass transfer and mass transport and require longer times for rebound.

Conversely, ground-water samples collected immediately after ISCO deployment may be useful for operational evaluation. For example, ground-water samples containing significant contaminant concentrations indicate hot spot areas that will likely require additional oxidant. Therefore, decision-making and additional oxidant injections could occur before rebound is fully developed and documented. However, nondetect or low concentrations of the contaminants in ground-water samples are generally inconclusive until sufficient time has been allowed for rebound. Ground-water sampling immediately after ISCO may provide an early warning for metals mobilization. Attenuation of mobilized metals is time dependent and subsequent sampling may be necessary to assess transport and potential exposure pathways.

Ground-water samples collected for analysis of contaminants that contain the oxidant should be avoided. The oxidant could interfere with analysis of the ground-water sample or could continue reacting with the contaminant(s) and interfere with data interpretation. In the case of MnO_4^-, reductants are added to react with MnO_4^- and eliminate the oxidant (e.g. sodium thiosulfate, sodium bisulfite). Ground-water sampling and analysis for contaminants after the oxidant has fully reacted is recommended.

Ground-water monitoring wells, piezometers, or temporary well points can be used to measure direct and/or indirect parameters of treatment performance. Performance monitoring will require ground-water samples collected from monitoring wells that are appropriately constructed and strategically placed. Sentry wells may be used to assess contaminant transport after ISCO. This is especially applicable to Fenton systems where various enhanced transport mechanisms could result from H_2O_2 injection (refer to Section II.C.2.h. Disadvantages). Pre- and post-oxidation monitoring of injection wells may provide useful information on treatment performance. However, optimal ISCO treatment performance will occur near the injection well. Consequently, ground-water contaminant and reaction byproduct concentrations will be low, and high, respectively, in ground-water samples collected from injection wells. Ground-water monitoring data representative of an injection well should be qualified for this reason.

III.E.4.b. Aquifer/Soil Sampling

The majority of contaminant mass in source areas where ISCO is deployed is present as NAPL or sorbed in the solid phase. Extraction and analysis of aquifer material and soil samples collected immediately after oxidant consumption may potentially provide rapid feedback on ISCO treatment performance and spatial distribution of contaminants. A delay in sampling for contaminant rebound is not necessary for these samples. Numerous pre- and post-oxidation soil core samples, distributed horizontally and vertically, are often required to quantify the spatial distribution of DNAPL and to assess whether significant reduction in treatment was accomplished. Accumulation of DNAPL on distinct lithologic units may result in a predictable pattern of DNAPL distribution. Under this condition, pre- and post-oxidation contaminant characterization is more straightforward and economically feasible.

III.E.4.c. Other

Due to the heat and O_2(g) released during H_2O_2 injection, volatilization of organic contaminants is highly probable. Therefore, performance monitoring at in-situ Fenton oxidation sites may involve monitoring volatile emissions. The extent of volatilization during in-situ Fenton oxidation has not been adequately investigated. Volatile releases, especially from source areas containing DNAPL or fuels, represent a high potential for volatilization, exposure pathways, and health and safety hazards. Volatilization may also result from the sparging effect that occurs during in-situ ozonation especially if air sparging/injection is a component in the treatment process. O_3 itself is a hazardous oxidant and human contact and inhalation could have serious health effects. Until these potential exposure pathways can be documented and evaluated, volatile and O_3 emissions should be measured, controlled, and captured. Correspondingly, soil vacuum extraction, soil vapor, soil gas pressure, and off-gas monitoring may be needed. This should be evaluated on a case-by-case basis.

Elevated temperatures and pressures during H_2O_2 injection can result in the release of steam and volatile emissions during ground-water monitoring (i.e., opening of monitoring well caps). To avoid this potential health and safety hazard, sufficient time should elapse to allow the release of O_2(g), dissipation of pressure, and reduction in temperature.

III.E.4.d. Process and Performance Monitoring

Process and performance monitoring parameters are summarized in Table 13.

III.E.5. Summary of Contaminant Transport and Fate Mechanisms during ISCO

During ISCO, there are several transport and fate mechanisms that may occur simultaneously with

Table 13. Process and Performance Monitoring Parameters

Parameter	Purpose of the Data/Information
Process Monitoring	
Target Contaminant	Existence or persistence of the target contaminant can be used to determine where to design the spatial delivery of the oxidant.
Oxidants (H_2O_2, MnO_4^-, $S_2O_8^{2-}$, O_3)	Estimate radius of influence of oxidant injection; Evaluate oxidant distribution; Calculate reaction kinetics to help design monitoring program.
Metals	Assess whether redox- and/or pH-sensitive metals are mobilized; Assess attenuation of mobilized metals.
Fe, Phosphate, Chelators	Assess radial influence/distribution of injected reagents.
pH	Assess whether pH is optimal; Assess impact of acid injection/pH modification.
Alkalinity/Buffer Capacity	Anticipate acid requirements for pH modification.
E_h (electrode potential)	General indicator of oxidant distribution.
Ground-Water Level	Assess hydraulic connection between injection monitoring wells and potential transport pathways.
Performance Monitoring	
Target Contaminant	Assess treatment performance via reduction in concentrations and/or mass in ground water, aquifer material, and NAPL; Assess whether cleanup objective is being achieved and if the site can be closed; Monitoring soil gas or off-gas reveals the fate and transport and potential exposure pathways of volatile organics; Assess changes in the plume dimension.
Reaction Byproducts	Confirm the presence and transformation of the target compound(s); Estimate the mass of contaminant transformed (for example, oxidation of chlorinated organic compounds releases Cl^-); Evaluate the presence of sorbed and non-aqueous phases; Assess secondary MCLs.

oxidation. The role of these mechanisms should be evaluated on a site-specific basis. In some cases, these mechanisms can be desirable, i.e., enhanced mass transfer. In other cases, it is not desirable (i.e., volatile losses, exposure pathway, health risk, etc.), and appropriate steps should be taken to minimize the impact. CO_2 (g) production during permanganate oxidation in heavily contaminated zones may mobilize NAPL and transport NAPL vapors (Reitsma and Marshall, 2000). Fenton oxidation involves the most complex range of transport and fate mechanisms of the oxidants (Figure 8). Thermal effects resulting from the Fenton reaction enhance the fate and transport mechanisms listed below.

Transport mechanisms

- Advective transport of contaminants in ground water results from ground-water displacement during injection, ground-water transport under natural and/or an induced gradient, and pneumatically-driven ground-water movement from O_2(g) production/expansion.
- Diffusive transport of contaminants in ground water from high to low concentration is influenced by ISCO activities/mechanisms.
- NAPL transport may result from changes in the hydraulic gradient attributed to ISCO activities.
- Advective and diffusive transport of volatile organics in the gas phase. Enhanced transport of volatile emissions due to O_2(g) evolution during Fenton oxidation.

Fate mechanisms

- Oxidation of dissolved, sorbed, and NAPL phase organic contaminants (i.e., the treatment objective).
- Transport of volatile compounds into the unsaturated zone/atmosphere represents the phase transfer of contaminants rather than a destructive loss mechanism.

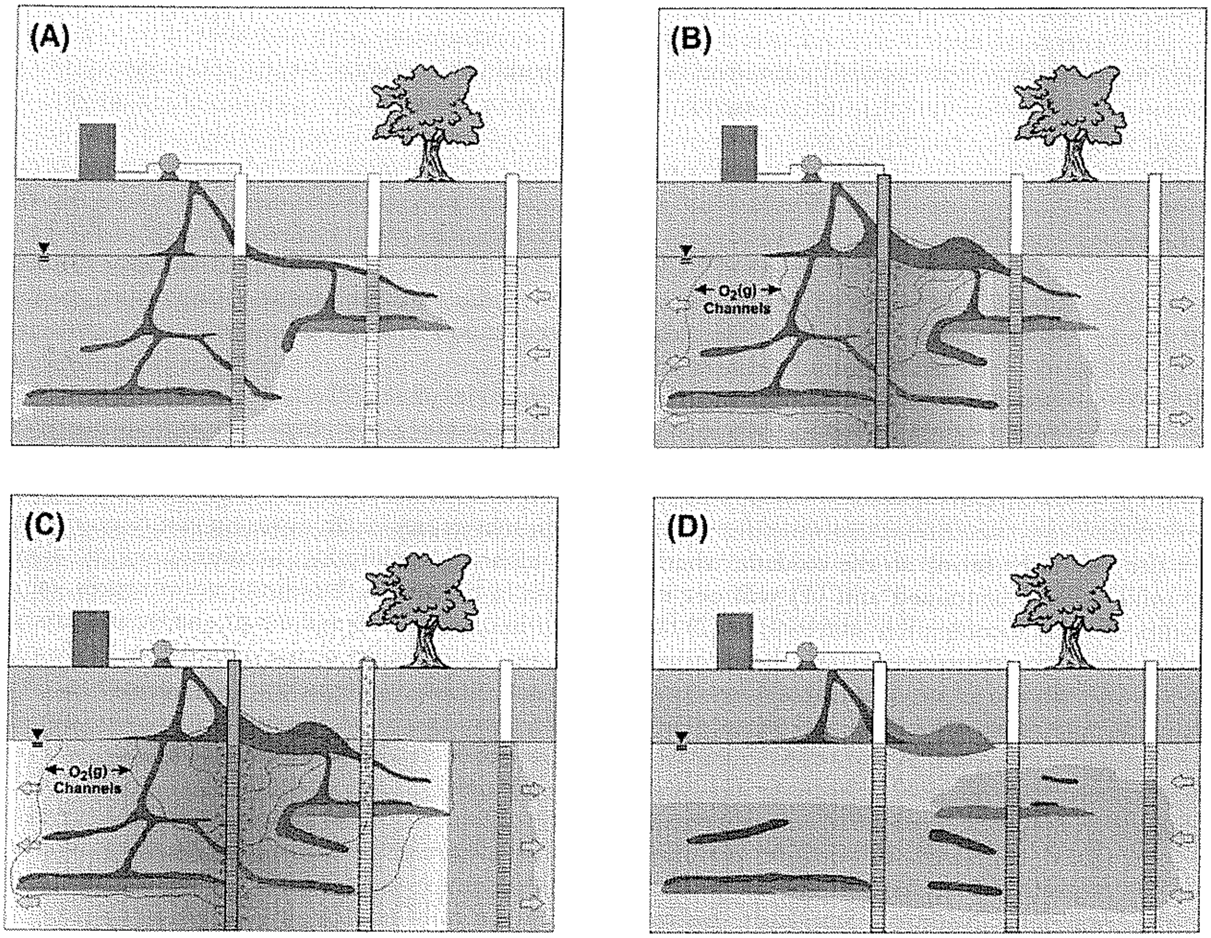


Figure 8. Conceptual model of in-situ Fenton oxidation and potential fate and transport mechanisms. (A) Cross-section of hazardous waste site containing DNAPL in the saturated and unsaturated zones. Injection well is constructed in the source area and two monitoring wells located in the upgradient direction (downgradient monitoring wells not shown); (B) H_2O_2 is injected and reacts producing heat and $O_2(g)$. Contaminants are transformed via oxidation and other possible mechanisms (reductive transformation, hydrolysis). The pneumatic pressure from the $O_2(g)$ and from H_2O_2 injection results in mounding of the ground water and displacement of the ground water away from the injection point. DNAPL movement, and enhanced volatilization of contaminants by $O_2(g)$ sparging + heat may also occur; (C) $O_2(g)$ sparging of the ground water in monitoring wells, artesian conditions, and continued ground-water displacement and enhanced volatilization may occur; (D) H_2O_2 injection ceases and is fully reacted. Loss of the target contaminant(s) in the source zone is achieved by oxidation transformation but may not be differentiated from other fate and transport mechanisms. Contaminant mass transfer and transport results in rebound.

- Biodegradation may occur under pre- and post-oxidation conditions.
- Sorption (adsorption, desorption) is impacted by changes in the contaminant concentrations in either the ground water and/or aquifer materials.
- Dissolution of organics from NAPL into the ground water.
- Hydrolysis (and possibly other abiotic reactions) is a destructive mechanism for organic contaminants.

III.E.6. Safety Issues

H_2O_2, MnO_4^-, $S_2O_8^{2-}$, and O_3 are all strong oxidizing agents and should be handled using appropriate methods and personal protective equipment to prevent the risk of chemical burns, fire, and explosions. Oxidant compatibility with all materials used in the remediation process should be reviewed and evaluated to minimize equipment deterioration, leaks, and failure. Health and safety plans (HASPs) should be reviewed by persons involved in the oxidant handling and other on-site ISCO procedures. A Project Safety and Occupational Health Officer (or equivalent) should review field operation plans and personal protection equipment or other procedures that will protect worker safety and health while handling these oxidizers. Oxidant manufacturers provide up-to-date materials on compatibility, handling, storage, and health and safety information. Such information is easily accessible on manufacturers' websites. All on-site personnel should be trained according to the requirements specified in 29 CFR 1910.1200 (h) (OSHA's Hazard Communication Standard) for the specific oxidizer. Materials safety data sheets (MSDS) can provide useful information regarding health and safety issues and should be on-site when the work is performed. Coordination with local emergency response service providers will assure they are prepared in the event of a spill/release emergency.

The work site should be set up so the oxidant, whether liquid or solid, will be contained and (1) will not mix with organics or other incompatible material, or (2) flow uncontrolled into the environment (i.e., lake, stream, etc.) if an accident were to occur. Protective safety equipment including a portable eyewasher and shower could be used assuming an accidental exposure to oxidant(s) or other reagents occurred. These should be set up on site where oxidizers and other chemical materials will be handled or potentially contacted by on-site personnel. Standards for protective safety equipment are available through the American National Standards Institute (ANSI) (i.e., ANSI Z358.1-1998, Eyewash and Showers). O_3 generation equipment and associated plumbing should be operated and maintained in the open air or a well-ventilated building/temporary structure so that O_3 from a leak or improperly operated equipment cannot build up to levels that will be hazardous to workers. The storage of liquid and solid oxidizers should comply with standards established by the National Fire Protection Association (NFPA 430: Code for the Storage of Liquid and Solid Oxidizers) (NFPA, 2006).

A fatal dose of permanganate ingestion for an adult has been estimated to be 10 g (Carus Chemical Company, 2004), however, deleterious effects will occur from ingestion of much lower doses. The characteristic pink color of MnO_4^- can be observed at low concentrations (several mg/L), providing an easy detection method and prevention of potential exposure pathways. Precautions should be taken to prevent inhalation of $KMnO_4$ dust during handling and mixing. Commercially available permanganate mixing equipment can be used to minimize potential exposures to the oxidant. Skin and eye contact, and ingestion of MnO_4^- must also be avoided. Unused oxidant solution should be neutralized by a reductant such as sodium thiosulfate or sodium bisulfite. Neutralization chemicals should be available when the oxidant is delivered to the site. Due to the potentially violent reactivity (especially at higher sodium permanganate solution concentrations), the neutralization should be conducted carefully, using adequate safety precautions. Serious burns to an individual resulted from an accident in 2000 during ISCO at the Portsmouth Gaseous Diffusion Plant, Piketon, OH in which sodium thiosulfate was improperly added to a concentrated $NaMnO_4$ solution.

Reactions involving H_2O_2 are exothermic and release large volumes of $O_2(g)$, especially at high H_2O_2 concentration. This reaction (and O_3 sparging) can result in enhanced volatilization and dispersal of organic vapors which may represent an exposure risk or an explosion or fire hazard. Specifically, accumulation of flammable vapors in basements, buildings, crawl spaces, etc., could result in unacceptable indoor air quality and exposures to humans, or explosion or fire hazards. In 1997, an explosion and fatality was reported in Wisconsin at a residence near a chemical oxidation project at a petroleum-contaminated site where gasoline vapor migration had occurred in sewer lines.

O_3 has adverse respiratory effects, and exposure to harmful levels must be avoided. O_3 injected during ISCO should be fully reacted in the subsurface. O_3 released into the air could be inhaled by site workers or others in the area. O_3 monitoring in air at the ISCO site should be an integral component to the routine monitoring to prevent unacceptable exposures. Additionally, O_3 production, storage equipment, and delivery lines should be monitored routinely for leaks through appropriate detection and pressure testing procedures.

$Na_2S_2O_8$ can decompose in storage under conditions of moisture and/or excessive heat, causing release of oxides of sulfur and O_2 that support combustion. Decomposition could result in high-temperature conditions. Airborne persulfate dust may be irritating to eyes, nose, lungs, throat, and skin upon contact and may cause difficulty in breathing (FMC, 2006). A review of potentially incompatible ISCO materials (with $Na_2S_2O_8$) should be performed prior to use of this oxidant.

III.E.7. Treatment Trains

Treatment trains involving other technologies used before, during, or after ISCO can be used to enhance treatment performance.

NAPL Removal: Removal of NAPL prior to ISCO is an important first step in source area treatment and is generally more efficient and effective than ISCO. This will decrease the mass of oxidant required for contaminant destruction. Additionally, this will increase the NAPL surface area for chemical oxidation, reduce the potential mass transfer limitations that results from $MnO_2(s)$ deposition at the NAPL interface, and reduce NAPL mobility during ISCO. Different technologies have been developed for the purpose of NAPL removal (Newell *et al.*, 1995; API, 1996; U.S. EPA, 1996; U.S. EPA, 2001b).

Excavation: Soil excavation of heavily contaminated soils may be a viable option at some sites to reduce contaminant mass and leaching of contaminants to ground water. The topographical depression in the subsurface may also serve as an infiltration trench for the delivery of oxidant to contaminants residing at lower elevations.

Soil Vapor Extraction (SVE): SVE can be used prior to ISCO to control, capture, and remove volatile organics from the unsaturated zone. Prior to permanganate injection at the Union Chemical Company Superfund Site (South Hope, ME), SVE was used to remediate the unsaturated soils (Connelly, 2003). Remedial objectives for SVE are to remediate the unsaturated zone and to prevent recontamination of ground water during/after ISCO. Due to the enhanced volatilization effects that occur during in-situ Fenton oxidation and O_3 sparging, SVE could be used to prevent volatile emissions, reduce exposure pathways, and minimize uncontrolled loss and accumulation of flammable vapors. SVE can also provide better distribution of O_3 in the unsaturated zone.

Oxidation:Reduction: Contaminant mixtures may be comprised of chemicals that are not entirely vulnerable to oxidation. Under this condition, another reaction mechanism such as reductive transformation may be needed to fully transform the contaminant mixture. Sequencing oxidation and reduction reactions, or, reduction and oxidation reactions, may be needed. Chemical reduction using dithionite followed by chemical oxidation (H_2O_2 and Fe) was laboratory-tested for a mixture of halogenated alkanes, halogenated alkenes, and aromatics (Tratnyek *et al.*, 1998). Dithionite is a reductant that reduces Fe(III) to Fe(II). Subsequently, carbon tetrachloride (CT) is reductively transformed via Fe(II), but is poorly oxidizable by chemical oxidants. Ideally, dithionite is used first to reductively transform CT, and is followed by Fenton oxidation to transform the other contaminants. However, it proved difficult to achieve successful results with the sequential application of reductant and oxidant due to the reaction between the oxidant and residual reductant. The sequential application of reductants and oxidants, and vice versa, involves a broad range of competing redox reactions. Ideally, this approach has a wide range of application, but is not currently a well-developed technology.

Bioremediation: Sequencing oxidation and reduction reactions may be achieved through biological reductive treatment. Electron donor reagents (i.e., hydrogen releasing compounds, lactate, vegetable oil, etc.) injected into the subsurface can biologically produce reducing conditions and reductive transformations. One site where carbon sources were injected to create an anaerobic reductive dechlorination environment after permanganate ISCO was the Union Chemical Company Superfund Site near South Hope, ME (Connelly, 2003; ITRC, 2005).

Enhanced or naturally occurring reductive transformation of oxidation-resistant compounds may occur downgradient from the ISCO area provided that sufficient separation can be achieved to allow the predominant redox zones to develop. Post-oxidation enhanced bioremediation may include aerobic biodegradation or aerobic cometabolic biodegradation with addition of co-substrates. Site-specific feasibility testing is necessary to address the uncertainties of sequential oxidation and bioremediation.

It is anticipated that in nearly all cases, natural attenuation will be an integral component to ISCO because it is not economically feasible for ISCO alone to achieve the low cleanup standards specified at many sites for the source area, and/or for the entire plume (refer to Section III.F.5. Impact of ISCO on Natural Attenuation and Biodegradation).

Oxidant Combinations: H_2O_2 is a reactant of $S_2O_8^{2-}$ that produces the sulfate radical and may be injected as an activator during in-situ persulfate oxidation. Injected H_2O_2, a low cost oxidant, will react with naturally occurring Fe(II) to form ·OH and oxidize contaminants, and will oxidize reduced aquifer materials, thus lowering the TOD. This pre-treatment step would lower the reaction rate and oxidant demand for MnO_4^- and may be more cost effective.

The sequential injection of persulfate and permanganate was intended to satisfy the NOD with $S_2O_8^{2-}$ and oxidize the VOCs with MnO_4^- (Droste *et al.*, 2002). The intent of this approach was to minimize the amount of MnO_4^- required to meet the treatment objectives, and subsequently to minimize the accumulation of $MnO_2(s)$ and the potential for permeability loss. However, it was unclear to what extent TCE, DCE and VC were oxidized. The use of combining oxidants requires further investigation, since the impact of persulfate on NOD is unclear. Others have reported that persulfate is relatively unreactive toward naturally occurring organic matter (Brown and Robinson, 2004).

Ground-Water Pumping: Ground-water recirculation (and oxidant replenishment) or simply ground-water extraction can be used during ISCO to enhance the transport rate and direction of the injected oxidant. Ground-water pump-and-treat may be used to control and contain the migration of contaminants and the injected oxidant, to improve delivery of the oxidant, or to prevent migration to potential receptors.

Thermal Treatment: Thermal treatment, such as radio frequency heating, is likely to be necessary to heat the subsurface sufficiently so that thermally-activated persulfate oxidation can be effective (Liang *et al.*, 2001). The use of solar energy may also serve to economically heat the ground water in warm climate regions.

III.F. Limitations/Interferences/Impacts

III.F.1. Untreated COCs/Rebound

Organic chemicals that are poorly reactive with specific oxidants will persist in the ground water (Table 2). However, these compounds may be vulnerable to other remediation technologies (refer to Section III.E.7. Treatment Trains) or may attenuate naturally with acceptable risk. Persistence of the organic chemicals may also be due to insufficient delivery of oxidant. Causes of insufficient delivery include (1) reactive transport and consumption of the oxidant prior to fully reaching the target zone, (2) underestimating the total oxidant demand, and (3) delivery of oxidant to non-targeted zones. Good site characterization and performance monitoring are needed to determine why contaminants persist and to take steps to assure adequate oxidant delivery.

Contaminant rebound involves the condition in which contaminant concentrations in the presence of oxidants are low or nondetectable, but steadily increase (rebound) in the ground water after oxidant concentrations have diminished. Rebound is attributed to extended periods of slow mass transfer and mass transport mechanisms of the residual contaminants. These mechanisms include the slow dissolution of contaminants from NAPL or through $MnO_2(s)$ precipitate on NAPL, slow desorption from aquifer materials, slow advective transport in ground water, and slow diffusive transport of contaminants usually from low-permeability materials. If monitoring wells are not located near the source zone/ISCO area, the prolonged time required for ground-water transport, sampling, and detection of contaminants can be delayed and contribute to rebound. In Fenton systems, $O_2(g)$ entrapped in porous media may also interfere with ground-water flow, mass transport, or mass transfer.

Few sites where ISCO has been implemented, if any, have achieved the treatment objectives in a single application. Because of the high probability of rebound, multiple applications should be budgeted and planned. In general, this involves an iterative approach of monitoring diagnostics and reapplications of the oxidant (refer to Section III.E.2. General Conceptual Approach). Rebound underscores the importance of establishing an efficient monitoring well network, long-term monitoring, and multiple oxidant applications.

III.F.2. Toxic Reaction Byproducts

Metals: An increase in heavy metals concentration in ground water may result from heavy metals impurities contained in the permanganate, and mobilization of pre-existing redox- or pH-sensitive heavy metals (in-situ) by the oxidant. Field investigations generally reveal that these metals attenuate through various mechanisms and within acceptable transport distances (refer to Section II.C.1.f. Metals Mobilization/Immobilization).

Organics: Reaction byproducts are generally less toxic, more biodegradable, and more mobile than the parent compound. For example, reaction byproducts from the oxidation of MTBE by Fenton's or persulfate include *tert*-butyl formate, TBA, and acetone (refer to Section II.C.2.b. Contaminant Transformations). Ketones (e.g., acetone) and alcohols are reaction byproducts from the oxidation of petroleum hydrocarbons by MnO_4^- (Fatiadi, 1987). These byproducts may not be acceptable and should be monitored and evaluated on a site-specific basis. Further transformation of reaction byproducts is possible, assuming sufficient oxidant is available. Enhanced biodegradation and/or natural attenuation may be feasible and acceptable under some conditions.

Other: Nitrate (NO_3^-) is one of the nitrogen byproducts from the oxidation of high explosives HMX and RDX (Zoh and Stenstrom, 2002). Oxidation of high concentrations of these contaminants could potentially result in the accumulation of NO_3^- in excess of the U.S. EPA maximum concentration level (10 mg/L, as nitrogen).

III.F.3. Process Residuals

Process residuals from $KMnO_4$ can include a sludge that accumulates in mixing, storage, or distribution tanks.

The sludge may contain water-insoluble sand/silica solids that are additives to "free-flowing" grade of dry oxidant granules to prevent clumping during handling. The sludge may also include $MnO_2(s)$ and particulate permanganate ($KMnO_4(s)$). Causes for $KMnO_4(s)$ include (1) inadequate mixing of the oxidant solution, (2) exceeding the solubility of MnO_4^- during preparation, and (3) reductions in temperature during storage (i.e., this lowers the $KMnO_4$ solubility, resulting in precipitation reactions). Injection or precipitation of $KMnO_4(s)$ can cause permeability reductions in or near the injection well. However, given sufficient time, $KMnO_4(s)$ will dissolve into the aquifer. Redevelopment of a well may be needed to restore the permeability where the responsible mechanism is not reversible under ambient conditions.

III.F.4. Geochemical Impacts

The immediate geochemical impact of injecting oxidants is to increase the oxidation state of the aquifer. Oxidation reactions change the solubility of many inorganic species, resulting in the precipitation of soluble mineral species. The four most common reduced inorganic species are Fe, Mn, As, and sulfides (Brown and Robinson, 2004). Long-term post-oxidation rebound in reducing conditions, possibly through microbially-driven reactions, results in the dissolution of precipitated (solid phase) minerals. The extent to which this pattern of redox conditions and geochemical reactions occurs is dependent on site-specific conditions. The elements O, S, Fe, and Mn are injected at high concentrations during ISCO and are predominant participants in ground-water redox processes. Secondary effects from the injection of these oxidants include the geochemical impact by enhanced microbial activity (refer to Section III.F.5. Impact of ISCO on Natural Attenuation and Biodegradation). Numerous site-specific inorganic and organic reactants exist in the subsurface that strongly influence a wide range of geochemical outcomes. It is beyond the scope of this Engineering Issue Paper to address the complex and broad nature of geochemical impacts of ISCO. Probable chemical reactions and byproducts involving these elements are covered in detail elsewhere (Stumm and Morgan, 1996). The long-term geochemical impact of these oxidants and reagents has not been well-documented.

III.F.4.a. Oxidants

After oxidation is complete (i.e., MnO_4^- reacted), $MnO_2(s)$ and Mn^{+2} are the predominant manganese species. $MnO_2(s)$ can be found under a wide pH range (pH 2 to 14) and will likely be the predominant form of manganese. $MnO_2(s)$ can dissolve under reduced conditions (pH <8), resulting in an increase in Mn^{+2} in the ground water. The persistence of $MnO_2(s)$ or the impact of Mn^{+2} in aquifers have not been rigorously established; however, dissolution under reducing conditions in sediment/surface water systems has been reported (Hem, 1985; Drescher *et al.*, 1998). At pH >8, various manganese solid phase minerals (oxides, hydroxides, carbonate species) form. Mobilized manganese species (Mn^{+2}, colloidal $MnO_2(s)$) could be an aesthetic concern in drinking water if recovered in water-supply wells (refer to Section II.C.1.g. EPA Drinking Water Standard). $MnO_2(s)$ may impact NAPL mass transfer and permeability, and serve as a sorbent for heavy metals (refer to Sections II.C.1.e. Impact of $MnO_2(s)$ Accumulation and II.C.1.f. Metals Mobilization/Immobilization).

In general, in-situ Fenton oxidation involves injection of large quantities of H_2O_2, injection of various chemical reagents, and release of heat and $O_2(g)$ in the subsurface. After H_2O_2 is fully reacted, the predominant residuals in the injection zone are dissolved oxygen, $O_2(g)$, and heat. Similarly, in O_3 oxidation, after O_3 is fully reacted, the predominant residuals are $O_2(g)$ and dissolved oxygen. In either case, $O_2(g)$ will slowly dissolve into the ground water and maintain elevated dissolved oxygen concentrations and redox conditions in the injection area. With Fenton oxidation, the heat will slowly dissipate and ultimately the site will return to ambient temperature. Although it is unknown how long these conditions will persist, the potential geochemical impact is site-specific and involves many potential reactions and mechanisms (refer to Section II.C.2.e. $O_2(g)$ Generation and Exothermic Reaction; Section II.C.2.f. Injected Reagents; and Section III.F.5. Impact of ISCO on Natural Attenuation and Biodegradation).

Persulfate oxidation results in high concentrations of SO_4^{2-} in the aquifer. Under reducing conditions, SO_4^{2-} can be reduced to sulfide (HS^-). Both SO_4^{2-} and HS^- are highly soluble and mobile in ground water. Elevated concentrations of these species in ground water could exceed the secondary drinking water standard (refer to Section III.D.3. Regulatory Constraints on Injection of Reagents). In calcium-rich environments, the mineral gypsum ($CaSO_4 \cdot 2H_2O$) may form which is a relatively insoluble form of sulfate.

III.F.4.b. Natural Organic Matter

Permanganate is most reactive with natural organic matter (NOM) of the four oxidants used in ISCO, and persulfate is relatively unreactive towards NOM (Brown and Robinson, 2004). The role of natural organic material in

Fenton-driven oxidation reactions has not been systematically investigated and remains uncertain. Watts *et al.* (1990) found that the ratio of pentachlorophenol (PCP) and H_2O_2 consumption rates in soil suspensions was inversely related to NOM, suggesting that NOM successfully competed with PCP (and H_2O_2) for ·OH. In a different study involving $FeSO_4$ and H_2O_2 addition, the oxidation of benzo(a)pyrene was inhibited by the presence of non-target organics including glucose, cellulose, and lignin (Kelley *et al.*, 1990). Conversely, humic acids promoted O_3 decomposition and ·OH formation, and any activity of humic acids as ·OH scavengers was offset by the enhanced formation of free radicals (Masten, 1990). Fenton-driven degradation of 2,4,6-trinitrotoluene was greater in a system amended with fulvic acid than in another containing humic acid. Enhanced kinetics was attributed to accelerated Fe(III) reduction (Li *et al.*, 1997). Fenton oxidation and ·OH production was enhanced in the presence of peat by one or more peat-dependent mechanisms (Huling *et al.*, 2001). Fe concentration and availability in the peat, reduction of Fe(III) to Fe(II) by the organic matter, and reduction of organic-complexed Fe(III) to Fe(II) were probable causes. Contaminated aquifer material containing this type of organic material may exhibit similar mechanisms that enhance Fenton oxidation. Humic material (i.e., NOM) can facilitate electron transfer for Fe(III) reduction in microbial systems (Lovley *et al.*, 1996; Scott *et al.*, 1998), and similar redox coupling can be provided by constituents of humic materials (quinones, hydroquinones) in Fenton systems (Chen and Pignatello, 1997). Such reactions may provide an additional mechanism for Fe(III) reduction to Fe(II), resulting in more efficient ·OH production.

It has been proposed that NOM is oxidized during ISCO, resulting in the release of sorbed contaminants. An apparent release of RDX from the sorbed phase was measured during $KMnO_4$ oxidation (Struse *et al.*, 2002b). Increased bioavailability of chlorinated compounds by NOM oxidation was proposed for the observed increased rate of biological reductive dechlorination (Droste *et al.*, 2002). A portion of sorbed PAHs were released from the oxidation of NOM by $S_2O_8^{2-}$ (Cuypers *et al.*, 2000). Additionally, a lag time was reported before TCE and TCA oxidation by $S_2O_8^{2-}$ and was attributed to the oxidation of soil organic carbon followed by contaminant transformations (Liang *et al.*, 2001; 2003). Overall, these studies suggest that NOM oxidation corresponds with a release (desorption) of compounds, especially those less amenable to oxidation, such as TCA. Consequently, a temporary increase in contaminant concentrations could result, but would decline from the application of additional oxidant.

III.F.4.c. pH

pH is a master variable in geochemical equilibrium and can be significantly impacted during ISCO either by injection of an acid reagent or by the acidity/alkalinity produced by chemical reactions. A decline in pH is generally undesirable due to the potential for enhanced transport of some pH-sensitive metals under acidic conditions. The magnitude, direction, and permanence of the pH change are dependent on the buffer capacity of the aquifer material, the amount and type of contaminant oxidized, and the mass of oxidant and/or acid injected. All of these parameters are site-specific, suggesting that pH changes that occur during ISCO can be varied.

Permanganate oxidation can affect the pH differently depending on the target analyte. Oxidation of PCE and TCE will lower the pH by release of H^+; and oxidation of DCE and VC raises the pH by release of OH^- (Table 3, reactions 4 to 7). The direction of pH change could therefore increase or decrease depending on the type and quantity of contaminants present (Siegrist *et al.*, 2001, and references therein).

PCE: 8 moles H^+ /3 moles PCE
TCE: 1 mol H^+/1 mol TCE
DCE: 2 mol OH^-/3 mol DCE
VC: 7 mol OH^-/3 mol VC

Reduction in pH is consistently observed as a result of ISFO. pH modification during ISFO can result from injecting acid to enhance Fenton oxidation (refer to Section II.C.2.f(3) Acidification), from the Fenton reactions (Table 4, reactions 1 to 3), and from the oxidation of organic compounds. Reduction in pH may also occur from the oxidation of organic compounds by $S_2O_8^{2-}$ (Liang *et al.*, 2001; Huang *et al.*, 2002) or O_3.

III.F.4.d. Cation Exchange Capacity

The cation exchange capacity (CEC) is a measure of the aquifer material's ability to adsorb exchangeable cations. Common cations include H^+, K^+, Na^+, NH_4^+, Ca^{+2}, Mg^{+2}, and Al^{+3}. Changes in ground-water chemistry caused by the injection of oxidants and from various chemical reactions can impact the CEC. For example, injection of $NaMnO_4$, $KMnO_4$, or $Na_2S_2O_8$ at high concentration may displace some of the common cations or possibly heavy metals. In porous media containing a high percentage of clay, displacement of cations by Na^+ (i.e., $NaMnO_4$, $Na_2S_2O_8$) could contribute to the dispersion of soil particles, elimination of macropores, and deterioration of soil structure making the media impervious to water penetration. Although reduction in permeability is rarely measured/reported in ISCO, the potential consequences of injecting high concentrations of sodium-based oxidants and excessive Na^+ in clay-rich environments should be evaluated.

III.F.5. Impact of ISCO on Natural Attenuation and Biodegradation

III.F.5.a. Impact on Natural Attenuation

Natural attenuation is expected to play an important role in the overall remedy at most sites where ISCO is deployed. Permanent inhibition of microbial activity by the injected oxidants is undesirable since biotic processes are an integral component in natural attenuation. However, H_2O_2, MnO_4^-, O_3, and $S_2O_8^{2-}$ are antiseptics and will inhibit or kill microorganisms at much lower concentrations than are typically used in ISCO. Additionally, oxidant-induced changes in redox potential and pH can also inhibit some microbial species. The post-oxidation decline in the diversity of microbial species suggests that some microorganisms are also sensitive to pH (Kastner *et al.*, 2000) or elevated redox potential and become inactive or die. Historically, H_2O_2 injection has been problematic for enhanced bioremediation due to rapid H_2O_2 decomposition, microbial toxicity, limited solubility of O_2, loss of $O_2(g)$ to the unsaturated zone (Spain *et al.*, 1989; Huling *et al.*, 1990; Pardiek *et al.*, 1992), reduction in permeability (Weisner *et al.*, 1996), and excessive heat.

Short-term laboratory oxidation studies involving complete-mix soil slurry batch reactors, and flow-through column studies allow complete hydraulic control and excellent contact between oxidant, aquifer material, and microbes. These testing conditions result in a high impact of the oxidant on microbial activity (Hrapovic *et al.*, 2005). Laboratory studies conducted in this manner provide insight into the potential effect of the oxidant on microbial activity. However, they do not fully represent the nonideal mechanisms and long-term time frames associated with ISCO under field conditions that strongly influence microbial survival and activity under harsh oxidative conditions. Differences between laboratory and field conditions help explain discrepancies between microbial inhibition results from laboratory studies and the seemingly low impact of ISCO on microbial activity at field-scale.

Preferential pathways in heterogeneous porous media result in hydraulic short-circuiting of the injected oxidants. Hydraulic short-circuiting and microniches prevent full contact between the oxidant and microbes, providing shelter and permitting the survival of microorganisms during rigorous applications of oxidants. Laboratory oxidation studies involving complete-mix soil slurry batch reactors allow excellent contact between oxidant, aquifer material, and microbes, which generally results in a high impact of the oxidant on microbial activity. Laboratory investigations are useful for several reasons and provide insight to the potential effect of the oxidant on microbial activity, but they do not fully represent the nonideal mechanisms under field conditions that strongly influence microbial survival under harsh oxidative conditions.

In sequential H_2O_2-driven oxidation and biodegradation, more extensive PAH and PCP degradation was measured than from biodegradation alone. An initial decline in the microbial population occurred after H_2O_2 (1 to 2%) was applied, but was followed by a significant increase a week later that surpassed the original microbial numbers (Allen and Reardon, 2000). In a field study where large volumes and high concentrations of H_2O_2 were injected, the abundance and activity of microorganisms declined, but rebounded in six months (Chapelle *et al.*, 2005). Microbial activity in TCE- and cis-1,2-DCE-contaminated soil and ground water was measured before and after treatment with $KMnO_4$ (11,000 gal., 0.7%) (Klens *et al.*, 2001). Two weeks after injection, the redox potential of the ground water was >800 mV and viable populations of anaerobic heterotrophs, methanogens, and nitrate- and sulfate-reducing microbes were present, but at lower levels than under pre-oxidation conditions. Three months after injection, the nitrate-reducing microbial populations had increased. Six months after injection, the redox potential of the ground water was about 100 mV, MnO_4^- was absent, and the aerobic heterotroph population in ground water had increased by several orders of magnitude greater than the pre-oxidation population. In other studies involving $KMnO_4$, the rate of biological reductive dechlorination of TCE increased after treatment (Rowland *et al.*, 2001), and no changes in the site's microbial community structure were measured (Azadpour-Keeley *et al.*, 2004). In three case studies involving the injection of high concentrations and/or large quantities of permanganate, ISCO did not sterilize the aquifer, nor was microbial activity permanently inhibited (Luhrs *et al.*, 2006). At one site, reductive dehalogenation of CVOCs following biostimulation with sodium lactate, and at the other two sites, a significant increase in the post-oxidation microbial biomass, and the post-oxidation presence of a viable and diverse microbial consortia capable of degrading a wide range of organic chemicals, were measured.

Sequential injection of $S_2O_8^{2-}$ and MnO_4^- was originally proposed to satisfy the natural oxidant demand with $S_2O_8^{2-}$, oxidize the VOCs with MnO_4^-, and minimize the amount of MnO_4^- required and the accumulation of MnO_2(s) (Droste *et al.*, 2002). It was unclear to what extent TCE, DCE, and VC were oxidized; however, monitoring data including reductive dechlorination daughter products, Cl^- mass balance, and measurements of H_2, SO_4^{2-}, dissolved iron, and phospholipid fatty acids, strongly suggested that enhanced reductive dechlorination had occurred. It was proposed this could have resulted from (1) increasing the amount of SO_4^{2-} and sulfate-reducing bacterial activity, (2) increased microbial activity due to simpler substrates from VOC oxidation, and (3) increased VOC bioavailability from the oxidation of sorbate (natural organic matter) (Droste *et al.*, 2002).

ISCO is often deployed in a source area which is generally small in size relative to the ground-water plume that extends downgradient. In the source area where the oxidant is injected, direct contact between the oxidant and microorganisms is possible and could inhibit microbial activity. Additionally, the elevation in redox potential can inhibit reductive dehalogenation activity until terminal electron accepting conditions shift back to iron- and sulfate-reducing conditions. Consequently, in systems where anaerobic and reductive transformations play a significant role, the post-oxidation impact of ISCO on natural attenuation would be greater and sustained than aerobic conditions. Reaction of the oxidant near the injection location (source area(s)) lessens the downgradient impact of the oxidant on microbial activity where polishing effects of natural attenuation occur.

A localized decline in microbial activity will result from direct contact between the oxidant and microbe, or from the highly oxidizing conditions. Microbes that are sensitive to oxidative treatments will decline in population and activity, while others that are insensitive to the change in redox potential may be unchanged or may respond favorably. Due to spatial separation between the source area where the oxidant is injected and downgradient areas, the impact of the oxidant may be low or nonexistent in downgradient microbially active areas. The length of time for "microbial rebound" is unclear, but given sufficient time after ISCO, microbial populations, microbial activity, and the rate of biodegradation increase, possibly to levels above pre-oxidation conditions. Proposed theories for increased bioactivity include improved bioavailability of trace constituents, lower concentration of challenging chemicals, more available simple substrate resulting from contaminant or natural organic matter oxidation, less competition (with other microbiota) for available nutrients and substrate, die off of microbial predators (Allen and Reardon, 2000), elevated temperatures, and more available terminal electron acceptors (TEAs). No cases were found where aquifer material was sterilized or where microbial activity had been permanently inhibited.

III.F.5.b. Mechanisms Which Potentially Enhance Biotically-Driven Natural Attenuation

Microorganisms obtain energy and carbon for new cell material through biochemical redox reactions in which electrons are transferred from organic contaminants to terminal electron acceptors. Under aerobic conditions, oxygen is the most energetically favorable TEA. However, due to the low solubility of oxygen, dissolved oxygen (DO) is rapidly depleted in ground water. Subsequently, anaerobic conditions may result where the biochemical oxidation of organic compounds continues to occur (Lovley and Phillips, 1986; Suflita *et al.*, 1988; Hutchins *et al.*, 1998). The sequential order of TEA utilization under anaerobic conditions is nitrate (NO_3^-), manganese (Mn(IV)), ferric iron (Fe(III)), sulfate (SO_4^{2-}), and carbon dioxide (CO_2). The TEAs O_2, NO_3^-, SO_4^{2-}, and CO_2 are generally found in the aqueous phase. Fe and Mn species and reducible organic matter are the primary sources of solid-phase TEA in aquifers (Heron *et al.*, 1994). The total TEA (aqueous + solid phase) available in the subsurface is predominantly attributed to the solid-phase fraction, and the aqueous phase constitutes a minor fraction (Huling *et al.*, 2002). Currently, the reducibility of aquifer organic matter is poorly understood and unquantifiable, and manganese species typically only contribute 2 to 5% of the total transferrable electron equivalents. Ferric iron is found in abundance and is present in the solid phase since it is slightly soluble in the near neutral pH range. In sulfate-rich environments, SO_4^{2-} may also be derived from aquifer sediments.

There are several mechanisms in which ISCO could be beneficial to natural attenuation. The exothermic reaction of H_2O_2 will raise the temperature and increase bioactivity. The injection of phosphate stabilizers during ISFO by some vendors introduces phosphorus, an essential element in the production of microbial energy and new cell material. Acidification resulting from the injection of acid or as a reaction byproduct may lower the pH and increase bioavailability of some microbial nutrients. The injection of each oxidant results in the addition of various TEAs including DO from H_2O_2 and O_3; SO_4^{2-} from $S_2O_8^{2-}$; and Mn^{+4} from MnO_4^-. The injection of Fe during ISFO also contributes to the total TEA, but is expected to be minor in most cases relative to the quantity of naturally occurring Fe. Oxidation of reduced aquifer sediments via H_2O_2 proceeds rapidly relative to microbially mediated decomposition (Barcelona and Holm, 1991; Korom *et al.*, 1996). Each of the oxidants involved in ISCO can oxidize the reduced TEAs (i.e., Fe^{+2}, Mn^{+2}, etc.) in the aquifer sediments. Therefore, while oxidant injection is intended for immediate contaminant oxidation and could result in short-term, localized microbial inhibition, it also introduces TEAs into the aquifer and oxidizes aquifer sediments. At one site, a shift from sulfate-reducing to Fe(III)-reducing conditions resulting from H_2O_2 injection may have decreased the efficiency of reductive dechlorination in the injection zone (Chapelle *et al.*, 2005). However, it could also shift the predominant terminal electron accepting process from an inefficient one (methanogenesis) to more efficient processes such as aerobic biodegradation and/or Fe, Mn, and SO_4^{2-} reduction (Huling *et al.*, 2002) and provide a sustained long-term source of TEA.

III.G. Summary

Over the last 10 years, significant development of ISCO has dramatically advanced the state of the science, state of the practice, and the effectiveness of this technology. ISCO has been used at thousands of hazardous waste sites in the U.S. and is the fastest growing subsurface remedial technology used today. Wide application of this technology under variable site conditions has provided valuable field experience. Such field experience in conjunction with continued research and development will improve both the state of the practice and state of the science. These improvements will include the identification of site-specific parameters needed to assess the feasibility of ISCO, the development of predictive tools that allow an improved assessment of the potential benefits and adverse effects prior to ISCO deployment. Ultimately, this will contribute to more effective and efficient use of the technology and lower remedial costs.

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VI. QUALITY ASSURANCE STATEMENT

All research projects making conclusions or recommendations based on environmentally-related measurements and funded by the Environmental Protection Agency are required to participate in the Agency Quality Assurance (QA) program. This project did not involve physical measurements and as such did not require a QA plan.

VII. ACRONYMS, ABBREVIATIONS, AND SYMBOLS

(g)	gas
(s)	solid
η	oxidation efficiency
AFB	Air Force Base

aq	aqueous
BTEX	benzene, toluene, ethylbenzene, xylene
CB	chlorobenzene
CEC	cation exchange capacity
CERCLA	Comprehensive Emergency Response, Compensation, and Liability Act
CF	chloroform
CHP	catalyzed hydrogen peroxide
cm	centimeter
COC	contaminant of concern
COD	chemical oxygen demand
CT	carbon tetrachloride
CVOC	chlorinated volatile organic compound
DCA	1,1-dichloroethane
DCE	dichloroethylene
DNAPL	dense nonaqueous phase liquid
DO	dissolved oxygen
EDTA	ethylenediaminetetraacetic acid
E_h	oxidation-reduction potential
EPA	U.S. Environmental Protection Agency
EPCRA	Emergency Planning and Community Right to Know Act
Eqn	equation
f_{oc}	fraction of organic carbon
ft	foot
g	gram
gpm	gallons per minute
HMX	octogen, or cyclotetramethylenetetranitramine (high explosive)
hr	hour
ISCO	in-situ chemical oxidation
ISFO	in-situ Fenton oxidation
kg	kilogram
kWh	kilowatt-hour
lb	pound
L	liter
LNAPL	light nonaqueous phase liquid
m	meter
MC	methylene chloride
MCL	maximum contaminant level
mg	milligram
MGP	manufactured gas plant
min	minute
mL	milliliter
MNA	monitored natural attenuation
mol	gram molecule
MTBE	methyl tertiary butyl ether
mV	millivolt
n	porosity
NAPL	nonaqueous phase liquid
NOD	natural oxidant demand
NOM	natural organic matter
NTA	nitrilo-triacetic acid
°C	degrees Celsius
ORNL	Oak Ridge National Laboratory
OSC	on-scene coordinator
OSHA	Occupational Safety and Health Administration
OU	operable unit
PAH	polynuclear aromatic hydrocarbon
PCB	polychlorinated biphenyl
PCE	perchloroethylene
PCP	pentachlorophenol
pH	negative log of hydrogen ion concentration
pK_a	negative logarithm of the acid dissociation constant, K_a
ppm	parts per million
psi	pounds per square inch, unit of pressure
PVC	polyvinyl chloride
RCRA	Resource Conservation and Recovery Act
RDX	cyclotrimethylenetrinitramine, (cyclonite), (hexogen), (T4), high explosive
RPM	remedial project manager
rxn	reaction
scfm	standard cubic feet per minute
SDWA	Safe Drinking Water Act
sec	second
SMCL	secondary maximum contaminant level
SVE	soil vapor extraction
TBA	tertiary butanol
TCA	1,1,1-trichloroethane
TCE	trichloroethylene
TEA	terminal electron acceptor
TOC	total organic carbon
TOD	total oxidant demand
U.S. EPA	United States Environmental Protection Agency
UIC	Underground Injection Control
UV	ultraviolet
V	volt
VC	vinyl chloride
VOC	volatile organic compound
WEF	Water Environment Federation
wt	weight

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