

TECHNOLOGY STATUS REVIEW

IN SITU OXIDATION



Environmental Security
Technology Certification
Program

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Table of Contents

Acknowledgements	iii
Acronyms and Abbreviations	iv
1 Introduction	1
2 Objectives	3
2.1 Phase I : Site Survey.....	3
2.2 Phase II : Site Profiles	3
3 Technology Description.....	5
3.1 Oxidation Chemistry.....	5
3.2 Application.....	6
3.3 Advantages.....	6
3.4 Concerns	6
3.5 Costs.....	7
4 Results	8
4.1 Phase I Site Survey.....	8
4.2 Phase II Detailed Site Profiles and Results	14
4.2.1 ISO Implementation.....	14
4.2.2 Site Results.....	14
4.2.3 Costs.....	16
5 Lessons Learned.....	29
5.1 Inferences Regarding the Impact of Site Conditions on the Success of an ISO Implementation.....	29
5.1.1 Conditions Associated With Successful Technology Implementation.....	29
5.1.2 Conditions Associated With Unsuccessful Technology Implementation.....	32
5.2 Considerations For Technology Implementation.....	34
5.2.1 Site Characterization Needs	34
5.2.2 Design Issues.....	34
5.2.3 Operational Issues	35
5.3 Additional Information Needs.....	35
5.3.1 Fate and Behavior of Oxidant	36
5.3.2 Design Issues for Field Demonstrations.....	37
6 References	40

List of Tables

Table 1	Summary of Phase I Survey Sites	9
Table 2	Characteristics of Phase I Sites.....	13
Table 3	Summary of Phase II Sites	18
Table 4	Summary of Soil Parameters at Phase II Sites.....	22
Table 5	Summary of Groundwater Data at Phase II Sites.....	23
Table 6	Summary of Design Parameters.....	25
Table 7	Summary of Performance Data.....	27
Table 8	State Target Cleanup Levels for Soil and Groundwater	39

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Acronyms and Abbreviations

ACO	Administrative Consent Order
AFB	Airforce Base
A/M Area	M – Area Hazardous Waste Management Facility
AOC	area of concern
ARAR	Applicable Relevant and Appropriate Requirement
avg.	average
BAT	Best Available Technology
bgs	below ground surface
BTEX	benzene, toluene, ethylbenzene, and xylene
cells/gdw	cells per gram dry weight
cfm	cubic feet per minute
cm/sec	centimeter per second
CO ₂	carbon dioxide
COE	Corps of Engineers
Conn.	Connecticut
CRREL	Cold Regions Research and Engineering Lab
CVOC	chlorinated volatile organic compounds
DA	disposal area
DCA	dichloroethane
DCE	dichloroethlyene
DCM	dichloromethane
DEP	Department of Environmental Protection
DNAPL	dense non-aqueous phase liquid
DO	dissolved oxygen
DOD	Department of Defense
DOE	Department of Energy
DRO	Diesel Range Organics
DSM	deep soil mixing
E ^o	oxidation potential
EPA	Environmental Protection Agency
ft	feet/foot

ft/day	feet per day
ft ²	square feet
g	grams
g/cm ³	grams per cubic centimeter
GDEP	Georgia Department of Environmental Protection
gm/day/well	grams per day per well
gpm	gallons per minute
GRO	Gasoline Range Organics
GW	groundwater
H ₂ O ₂	hydrogen peroxide
IAG	Interagency Agreement
in	inch
IRP	Installation Restoration Program
ISCOR	in situ chemical oxidation through recirculation
ISO	in situ oxidation
KMnO ₄	potassium permanganate
kPa	kilo pascal
lb	pound
LEAD	Letterkenny Army Depot
LNAPL	light non-aqueous phase liquid
l/min	liter per minute
M	million
m ²	square meter
m ³	cubic meter
MC	methylene chloride
MCL	maximum contaminant level
MEK	methyl ethyl ketone
mg/kg	milligram per kilogram
mg/L	milligram per liter
MnO ₂	manganese dioxide
MTBE	methyl tertiary butyl ethylene
mv	millivolt
NA	data not available
NAPL	non-aqueous phase liquid

NAS	Naval Air Station
NC	not conducted
NCDENR	North Carolina Department of Environment and Natural Resources
ND	not detected
NFESC	Naval Facilities Engineering Service Center
NHDES	New Hampshire Department of Environmental Services
NPL	National Priority List
NSB	Naval Submarine Base
O ₃	ozone
OBP	oil burn pit
ORNL	Oak Ridge National Laboratory
Ox./Red.	Oxidation/Reduction
PADEP	Pennsylvania Department of Environmental Protection
PAH	polycyclic aromatic hydrocarbon
PCB	polychlorinated biphenyl
PCE	perchloroethylene, a.k.a. tetrachloroethane
PCH	polychlorinated hydrocarbons
PDO	Property Disposal Office
POC	point of contact
PORTS	Portsmouth Gaseous Diffusion Plant
Pot.	Potential
ppb	parts per billion
ppm	parts per million
psi	pounds per square inch
RAC	Remedial Action Contract
RCRA	Resource Conservation and Recovery Act
R&D	research and development
ROI	radius of influence
SCFA	Subsurface Contaminants Focus Area
SE	Southeastern
S ₂ O ₈ ⁻²	persulfate
SRS	Savannah River Site
SWMU	Solid Waste Management Unit
s.u.	standard units

TCA	trichloroethane
TCE	trichloroethylene
TERC	Total Environmental Restoration Contract
TPH	total petroleum hydrocarbons
TVOC	total volatile organic compounds
USEPA	United States Environmental Protection Agency
USGS	United States Geological Survey
UST	underground storage tank
v	volts
VC	vinyl chloride
vfb	vent flow balance
VOC	volatile organic compounds
wt	weight
yd ³	cubic yards
ZOI	zone of influence
°C	degrees Celsius
\$/lb	dollars per pound
µg/l	micrograms per liter
µm	micrometer

1 Introduction

Soil and groundwater contamination with CVOCs is a widespread problem at DOD sites. ISO has been rapidly adopted as a remediation technology for CVOCs in both soil and groundwater. However, the technology has only recently been developed, and there is little operational history.

Sites contaminated with CVOCs have proven difficult and expensive to remediate, particularly when a DNAPL phase is present. On many sites these DNAPL accumulations are well below the water table, dispersed in very thin layers, difficult to find, and difficult to remove.

Currently, pump and treat and excavation are the only proven technologies for treating DNAPL; however, they both have limitations. Pump and treat operations can provide adequate containment, but removal of any CVOC source is very slow. The DNAPL accumulations serve as a long-term reservoir of contaminants, requiring that the pump and treat operations be continued indefinitely. Excavation can remove CVOCs in soil, but large amounts of clean soil must be moved and excavations have to be dewatered to remove DNAPLs below the water table. Therefore, these technologies can be very slow and/or very expensive.

Because there are many sites with CVOC contamination, there is a great need for cost effective and reliable in situ technologies. While few of these technologies have been carefully validated, vendors and site managers have been proceeding rapidly to at least test ISO.

ISO involves injection of strong oxidants into the contaminated subsurface, in some cases with other chemicals that function as catalysts. The oxidants chemically break down CVOCs upon contact to inert materials such as carbon dioxide, chloride and water. Chloroethenes are particularly susceptible to chemical oxidation. Several oxidants have been tried, but most commercial applications have used either hydrogen peroxide or potassium permanganate in the saturated zone and either hydrogen peroxide or ozone for the vadose zone.

The potential benefits from ISO include in situ contaminant destruction, relatively low cost, reliability, simplicity (as compared to in situ biological treatment) and rapid treatment. Like any in situ technology, site-specific constraints must be considered.

Oxidation is dependent on achieving adequate contact between oxidants and contaminants, and subsurface heterogeneities, preferential flow paths, and poor mixing in the subsurface can result in extensive pockets of untreated contaminants. Further, the reagents can be consumed by other oxidizable substrates (e.g., natural organic compounds or dissolved iron), limiting the efficiency of ISO treatment.

In situ oxidation has only been commercially practiced for the last 5-6 years. As a result, the technology is rapidly evolving and the state of the art has advanced considerably over time. The limitations of the technology are becoming better understood, and engineering approaches to overcoming some of these limitations have been developed. Although the chemistry involved is relatively simple, the technology is not a simple one to implement. The subsurface environment

can be difficult to control, and it can be difficult to get adequate distribution of the oxidants within the subsurface. Often, site-specific data is needed that may not be available from typical site characterization investigations. There have been significant improvements the ability to distribute oxidants within the subsurface and an improved understanding of the site-specific data needs.

This project was undertaken to survey several government sites, where ISO has been used, to do the following:

- help establish the basis for selecting and designing the technology;
- assess the costs and performance of the technology at specific sites;
- assess the reasons for success or failure of ISO; and
- provide guidance on the use of the technology, including data requirements, to allow site managers to use ISO with confidence.

This report attempts to capture the current state of the art for this very promising technology, recognizing it is in a state of rapid development. The report also attempts to indicate the types of information that are needed to continue the evolution of in situ oxidation and to successfully implement the technology at specific sites. By reviewing past projects, we hope to provide site managers with a better understanding of the conditions under which ISO should be used, realistic goals for the technology, and limited guidance on the data needs and best practices for its use at specific sites.

2 Objectives

The overall objective of this project was to assess the current status of ISO and to determine what additional information is needed to understand the site conditions for which ISO is appropriate. The project was conducted in two phases and the specific objectives for each phase are detailed below.

2.1 Phase I : Site Survey

The first phase consisted of a site survey to identify the following information:

- where ISO had been used;
- the scale at which it was deployed;
- the specific oxidants and vendors used; and
- an initial evaluation of its success or failure to meet the project objectives.

The site survey involved contacting ISO technology vendors and reviewing government databases and web sites (DOD, DOE, and EPA) to identify sites where ISO has been deployed. In most cases, site contacts were called to determine the following additional information:

- the current status of the project;
- the scale at which ISO was used;
- the contaminants and media treated;
- the responsible parties and regulators involved;
- the extent of any available site data; and
- the initial responses regarding the success or failure of the project.

The results of the Phase I survey were then used to select several sites for more detailed site profiles in Phase II.

2.2 Phase II : Site Profiles

The second phase consisted of further evaluation of selected Phase I sites and the development of site profiles. The evaluation consisted of a review of available site characterization, design, and performance data to investigate more fully and understand the following:

- the site conditions and the characterization available;

- the reasons why ISO was selected;
- the design parameters and rationale;
- the cost and performance of ISO under real-world conditions;
- the reasons for success or failure of ISO to meet the project objectives; and
- any specific technological concerns.

At the conclusion of the Phase II evaluation, the site information was summarized to develop some initial guidance on the selection and use of ISO, the lessons learned to date regarding the testing and use of the technology, and the key data gaps.

3 Technology Description

3.1 Oxidation Chemistry

The oxidation chemistry of CVOCs is relatively well-understood.^{1,2} Oxidants attack the C-C bonds in CVOCs. The double bonds that characterize chlorinated ethenes are far more reactive than the single bonds of chlorinated ethanes, so PCE and TCE are far more susceptible to oxidation than TCA for example. However, the chloroethanes are often claimed to be susceptible to oxidation as well. The current theory is that the oxidants cause formation of an unstable epoxide that then breaks down to yield ketones and aldehydes. These products may also be susceptible to further oxidation, to eventually yield carbon dioxide, water and chloride.

Several oxidants have been employed. For DNAPL sites, the most common oxidants used have been hydrogen peroxide (H_2O_2) and potassium permanganate (KMnO_4). Permanganate is more expensive than hydrogen peroxide, but it is more stable, and it is effective over a broad pH range. Ozone (O_3) is the strongest oxidant available, with an oxidation potential (E°) of 2.07v. However, ozone is a gas, and therefore most suitable for treating the vadose zone, or possibly LNAPL accumulations in the capillary fringe. Persulfate ($\text{S}_2\text{O}_8^{2-}$) salts are also available (although not reviewed as part of this document), with an E° of 2.01v, but these oxidants are relatively expensive and require thermal activation.

Hydrogen peroxide apparently works through two mechanisms: free radical generation and direct oxidation. The direct oxidation has an E° of 1.76 v, and free radical formation ($\text{H}_2\text{O}_2 = 2\text{OH}^\bullet + 2\text{H}^+ + 2\text{e}^-$) has an E° of 2.76v. The latter relies on so-called Fenton's chemistry, in which iron acts as a catalyst. Therefore, iron is often added with the hydrogen peroxide. In addition, pH adjustment is common because oxidation is more rapid under acidic conditions.

Permanganate has an E° of 1.70v and yields MnO_2 , an insoluble precipitate under most conditions. Catalysts and pH control are not needed for permanganate oxidation. The stoichiometry of complete oxidation reactions yields the following weight ratios for permanganate (expressed as KMnO_4 :CVOC): PCE (1.3:1); TCE (2.4:1); DCE (4.4:1) and VC (8.5:1). Of course, this stoichiometry ignores the oxidant demand due to other reduced compounds in the subsurface, which can be significant.

The advantages of peroxide as an oxidant include relatively low regulatory resistance, more field experience in its use than permanganate, and a sparsity of byproducts of oxidation.

Disadvantages include the need for pH control in some cases and difficulties controlling in situ heat and gas production. Permanganate has a lower cost than peroxide, it is more stable, and it is effective over a broad pH range. Oxidation also produces manganese oxides, which can precipitate and potentially cause reduced porosity. Increased dissolved manganese levels are also a potential regulatory concern, as is the purple color of groundwater containing unreacted permanganate.

Ozone has been used mostly for vadose zone treatment. It is less costly than permanganate or peroxide, but the most significant factor in choosing ozone is that it must be applied as a gas. Gases may disperse further in the unsaturated zone than a liquid, but vapor recovery and possible treatment can add considerable cost if it is required.

3.2 Application

In general, one application has been used, although several reinjections at intervals have been used for more thorough treatment. Recently, continuous injection using recirculation of amended waters has been used.

For single or multiple injections, permanent or temporary injection points are established, and an aqueous solution containing the oxidant and any needed catalysts is injected under pressure. The oxidant (and catalyst) concentration, the target pH, the injection well spacing (i.e., radius of influence), the number of injections, and the injection pressure are all important design parameters that can affect cost and performance.

The use of recirculation, with injection and extraction wells, is intended to increase subsurface mixing. The DOE has tried this approach with some apparent success. The costs are likely to be higher than even multiple injections without groundwater extraction and reinjection (with possible treatment required). However, the degree of mixing and therefore contact between contaminants and oxidant will be greater, leading to more complete treatment, especially in heterogeneous subsurfaces.

In some cases, mixing has been encouraged by use of injection arrays with thin screen intervals at different depths to fully saturate the target zone and limit the need for vertical migration of the oxidant. High injection pressures have also been used to create fractures in tighter subsurface materials, again to encourage migration and mixing of the reactants. Mixing has also been encouraged through the use of air injection, to “push” peroxide solutions out into the aquifer. Finally, in some cases vapor extraction has been used in conjunction with ISO in the vadose zone to relieve off-gas pressures, to encourage oxidant migration, and/or to capture any volatile emissions.

3.3 Advantages

The primary advantages of ISO technologies are their relatively low cost and speed. The cost of reagents is relatively low, so application of ISO is generally far less costly than other active source removal technologies, such as in situ thermal treatment or flushing using surfactants or co-solvents. Since the reaction is near-immediate, treatment is far more rapid than biological techniques, and can be faster than thermal or vapor recovery technologies.

3.4 Concerns

The primary concern is ensuring the health and safety of workers. Strong oxidants are corrosive, and potentially explosive. The design and operation of any ISO system must take into account the hazards of the chemicals and the potential for vigorous uncontrolled reactions in the subsurface.

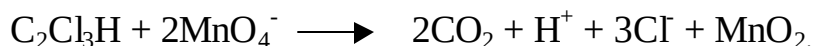
A significant performance concern is that the oxidation reaction is not complete, and significant DNAPL accumulations remain in untreated areas in the subsurface. Even a small percentage of the original DNAPL mass can result in a rebound in the groundwater concentrations after treatment to levels similar to those measured before treatment, or at least above levels of regulatory concern.

Another concern is the possibility of increased volatile emissions of CVOCs. Oxidation can cause significant heat generation and water vapor production. As a result, in situ steam stripping is a potential mechanism for contaminant loss, particularly for highly volatile compounds like CVOCs. For example, in cases where the hydrogen peroxide concentration exceeds about 11%, enough thermal energy can be released to cause water to boil, leading to a significant concern regarding vaporization losses.

A final concern is that there does not seem to be well-developed guidelines for the design and operation of ISO systems. The data needs for determining well spacing, screen intervals, or oxidant mass to be injected are not clear. There is a need for guidance to estimate the ROI under different conditions (soil texture, groundwater velocity, injection pressure, etc.). The efficiency of use of oxidants is not well-established, and guidance for determining the mass needed at a specific site does not seem to be available. Recommendations regarding operations and monitoring to prevent undesirable reactions (explosions, volatile emissions, or foaming) are also not clear.

3.5 Costs

Based on the stoichiometry in the equations for oxidation by peroxide and permanganate, the reagent costs for the oxidant alone are approximately 5 times lower for peroxide. Thus, using TCE oxidation as an example, the reactions are:



The resulting weight ratios (lb of oxidant per pound TCE fully oxidized) are 0.8 lb/lb for peroxide and 2.4 lb/lb for potassium permanganate. Typical costs are approximately \$1.10 per lb peroxide (normally sold as a 50% solution) and \$1.80 per lb for potassium permanganate. Therefore, the oxidant costs per pound of TCE destroyed would be \$4.32 for potassium permanganate and \$0.88 for 50% peroxide. Of course, peroxide use may also require additions of other reagents to acidify the subsurface or increase the iron concentration.

4 Results

4.1 Phase I Site Survey

A total of 42 ISO sites were identified during the Phase I Site Survey.

- Of the 42 sites, 17 were government and 25 were private facilities. Of the government facilities, 14 were DOD and 3 were DOE sites.
- Of the 42 sites, 19 were partially or primarily CVOC sites. Not surprisingly, the principal contaminants at the majority of the government sites were CVOCs, with TCE being the most prevalent contaminant of concern.
- Hydrogen peroxide was by far the most commonly used oxidant. It was used at 37 sites or 90% of the total sites. Potassium permanganate was used at only 4 sites, although it was used at 2 of the 3 DOE sites. Ozone was used at only one site
- The peroxide vendors included Geo-Cleanse, Clean-Ox, and ISOTEC. Clean-Ox was the largest vendor, with 16 sites total, although only 3 of these were DOD sites. Geo-Cleanse was the next largest vendor, with 13 sites total. However, they were the largest vendor at DOD sites (8 of the 12 DOD sites that used peroxide). ISOTEC was the smallest vendor, with 8 sites total, but only one DOD facility.
- Of the 14 DOD sites, pilot scale tests are in progress or completed at all. In addition, 5 of those sites have proceeded to full-scale remediation. Of the three DOE sites, all are considered demonstration projects, although one is listed as a full-scale demonstration. Of the 25 private sites, 10 have proceeded to full-scale.
- Of the 14 DOD sites, discussions with site contacts indicated that 6 were considered failures, including an explosion that terminated ISO operations at one site. At least 5 are proceeding to full-scale, indicating they were considered successful.
- None of the private sites were described as failures, but several site were described as successes (e.g., State issues No further Action letter) and several other pilot scale tests are planning to proceed to full-scale. However, even among the apparently successful sites, there is relatively little long-term data to judge the potential for rebound in groundwater concentrations. Furthermore, it is probably not surprising that failures are more likely to be reported at government sites than at private sites. Therefore, the extent of failure is probably more prevalent than these results indicate.

A summary of these sites is shown in Table 1 and a summary of site characteristics is shown on Table 2.

Table 1 Summary of Phase I Survey Sites

Site	Responsible Party	Project Status	Technology and Vendor	Scale	Regulatory Authority	Contaminants of Concern	Media	Point of Contact
Anniston Army Depot, Anniston, AL	DOD Army Corps of Engineers	Active to be complete in 99	Hydrogen Peroxide Geo-Cleanse	Pilot complete Full Scale underway	Unknown	TCE	Soil and Groundwater	Rick Levin 352-333-3633
US Army Cold Regions Research Lab, Hanover, NH	DOD Army Corps of Engineers	Active site will operate until 2000	Potassium Permanganate Corps of Engineers In-house project	Pilot complete Full Scale underway	Unknown	TCE	Soil and Groundwater	Daniel McKay 603-646-4738
Naval Air Station, Patuxent River, MD	DOD Navy Facilities Engineering Command	Project Complete Two Sites	Hydrogen Peroxide CleanOX	Pilot Scale at two sites	State UST Program Cleanup	BTEX	Soil and Groundwater	Dan Jordan 301-342-3030
Naval Station Roosevelt Roads, Puerto Rico	DOD Navy Facilities Engineering Command	Injection complete, sampling in progress	Hydrogen Peroxide Navy RAC Contract CleanOX	Pilot scale	RCRA fuel storage site	BTEX	Soil and Groundwater	Chris Penny 757-322-4815
Kiefer Park, Rhode Island	DOD Army Corps of Engineers	Project complete but not successful	Hydrogen Peroxide In house Corps of Engineers CleanOX	Pilot scale	No regulatory driver, it was a technology experiment	BTEX	Soil and Groundwater	Ian Osgerby 978-318-8613
Defense Logistics Agency Warehouse, New Cumberland, PA	DOD Army Corps of Engineers	Project in progress.	Hydrogen Peroxide Army Corps Contract ISOTEC	Pilot scale project Cleaning the base gas station	UST cleanup	BTEX	Soil and Groundwater	Sandy Bolinger 256-895-1467 Dale Glacker 717-770-8147
Naval Air Station, Pensacola, FL	DOD Naval Facilities Engineering Command	Project in progress.	Hydrogen Peroxide Navy RAC Geo-Cleanse	Full scale project	RCRA State requirement for source control	TCE	Groundwater	Maxi Kiesler 843-820-7322
Nellis Air Force Base, Las Vegas, NV	DOD Army Corps of Engineers	Project Complete	Ozone KV Associates	Pilot scale project	RCRA	TCE	Groundwater	Gene Lieu 402-221-7169
Shaw Air Force Base, SC	DOD Army Corps of Engineers	Project Complete	Hydrogen Peroxide Army Corps of Engineers Geo-Cleanse	Pilot scale project	RCRA	TCA and DCA	Soil and Groundwater	Ted Streckfuss 402-221-3826
Letterkenny Army Base, Letterkenny, PA	DOD Army Corps of Engineers	Three projects. Two are complete. Third begins in April 99	Hydrogen Peroxide Army Environmental Center Geo-Cleanse	Two pilot scale projects and one full-scale remediation.	RCRA	BTEX and Chlorinated Solvents	Bedrock Groundwater Soil	Paul R. Stone III 410-962-4906

Table 1 Summary of Phase I Survey Sites

Site	Responsible Party	Project Status	Technology and Vendor	Scale	Regulatory Authority	Contaminants of Concern	Media	Point of Contact
Naval Submarine Base, Kings Bay, GA	DOD Navy Facilities Engineering Command	Project is complete	Hydrogen Peroxide Navy RAC Geo-Cleanse	Full scale project	RCRA	PCE	Soil and Groundwater	Cliff Casey 843-820-5561
Marine Corps Air Station, Cherry Point, NC	DOD Navy Facilities Engineering Command	Project was a failure and was terminated	Hydrogen Peroxide Navy RAC Geo-Cleanse	Pilot scale project	State UST regulatory requirements	Gasoline, Waste Oil, Diesel, and Heating Oil	Soil and Groundwater	Steve Chambliss 757-322-4768
DOE Facility, Savannah River, Aiken, SC	DOE Field Demonstration SCFA Project	Project was competed in 1997	Hydrogen Peroxide Geo-Cleanse	Pilot Scale Project	RCRA, DOE Innovative Technology Program	TCE and PCE	Soil and Groundwater	Karen Vangelas 803-725-5223
DOE Facility, Piketon, OH	DOE Portsmouth Gaseous Diffusion Plant	Project was completed in 1998	Potassium Permanganate	Full Scale Demonstration	RCRA, DOE Innovative Technology Program	TCE	Soil and Groundwater	Dr. Robert Siegrist 303-273-3490
DOE Facility, Kansas City, MO	DOE Kansas City Plant	Project was completed in 1996 sampling complete 1998	Potassium Permanganate	Field Demonstration of deep soil mixing	RCRA, DOE Innovative Technology Program	TCE and DCE	Soil and Groundwater	Steve Cline 423-241-3957
BMC Olen Site, Irvine, CA	Private Site Primary Contractor is ThermoRetec	Project is underway, 2 of 3 injections complete	Potassium Permanganate	Pilot Study complete, Full Scale underway	RCRA	TCE	Soil and Groundwater	
Sign Manufacturing Facility, Denver, CO	Private Site	Project was completed in 1997	Hydrogen Peroxide ISOTEC	Pilot and Full Scale	RCRA	BTEX	Groundwater	Andrew Schmeising 303-843-9700
Warehousing Facility, Union County, NJ	Private Site	Project completed in 1996	Hydrogen Peroxide ISOTEC	Pilot and Full Scale	State UST Program cleanup	MTBE and BTEX	Groundwater	Dr. Richard Watts 509-335-3761
Former News Publisher Facility, Framingham, MA	Private Site	Project completed in 1996	Hydrogen Peroxide CleanOx	Pilot and Full Scale	UST closure activity	TCA, DCE and Vinyl Chloride	Groundwater	Carl Shapiro 781-449-6450
Active Industrial Facility, Clifton, NJ	Private Site	Project completed in 1995-1996	Hydrogen Peroxide CleanOx	Pilot and Full Scale	Leaking UST Estimate of 600 gallons of solvent	TCA and VOCs	Groundwater	Michael Tumulty 973-942-0700
Truck Rental Facility, Oklahoma City, OK	Private Site Active Facility	Project completed in 1996	Hydrogen Peroxide ISOTEC	Pilot Scale	Leaking UST	BTEX and Free Product	Groundwater	ISOTEC POC, David Zervas 609-274-8500

Table 1 Summary of Phase I Survey Sites

Site	Responsible Party	Project Status	Technology and Vendor	Scale	Regulatory Authority	Contaminants of Concern	Media	Point of Contact
Manufacturing Facility Southern, CO	Private Site Active Facility	Pilot complete Full Scale is ongoing	Hydrogen Peroxide ISOTEC	Pilot and Full Scale	RCRA	PCE	Groundwater and Soil	ISOTEC POC, David Zervas 609-274-8500
Sussex County, NJ	Private Site Lakefront Property	Project Completed in 1997	Hydrogen Peroxide ISOTEC	Full Scale	Remedial Action	#2 Fuel Oil and TPH	Groundwater and soil	ISOTEC POC, David Zervas 609-274-8500
Southern, NJ	Private Site	Unknown	Hydrogen Peroxide ISOTEC	Full Scale	Former UST site	BTEX, Naphthalene	Groundwater	ISOTEC POC, David Zervas 609-274-8500
Quarry Facility Sussex County, NJ	Private Site	Project underway in 1998	Hydrogen Peroxide ISOTEC	Full Scale	RCRA remedial action	1,4-Dichlorobenzene, Naphthalene, 1,2-Dichlorobenzene	Groundwater	ISOTEC POC, David Zervas 609-274-8500
Aerospace Manufacturer Patterson, NJ	Private Site	Unknown	Hydrogen Peroxide CleanOx	Pilot Scale	Unknown	TCE and PCE	Groundwater and Soil	ManTech Environmental POC Ron Adams PE, 703-814-8366
Former Manufacturing Facility, Arkansas	Private Site	Unknown	Hydrogen Peroxide CleanOx	Pilot Scale	Unknown	TCE and 1,2-DCE	Groundwater	ManTech Environmental POC Ron Adams PE, 703-814-8366
Electronics Manufacturing Facility Cambridge, MA	Private Site	Pilot Completed	Hydrogen Peroxide CleanOx	Pilot Scale	Unknown	PCE and TCE	Groundwater	ManTech Environmental POC Ron Adams PE, 703-814-8366
Former Industrial Facility, Union City, CA	Private Site	Pilot Completed	Hydrogen Peroxide CleanOx	Pilot Scale	Unknown	VOCs	Groundwater	ManTech Environmental POC Ron Adams PE, 703-814-8366
Printing Facility, Kingsport, AR	Private Site	Pilot Completed	Hydrogen Peroxide CleanOx	Pilot Scale	Unknown	BTEX, MEK, and Acetone	Groundwater	ManTech Environmental POC Ron Adams PE, 703-814-8366
Maintenance Garage Merrick, NY	Private Site	Pilot Completed	Hydrogen Peroxide CleanOx	Pilot Scale	Unknown	BTEX and MTBE	Groundwater	ManTech Environmental POC Ron Adams PE, 703-814-8366
Manufacturing Facility, Beloit, WI	Private Site	Pilot Completed	Hydrogen Peroxide CleanOx	Pilot Scale	Former UST site cleanup	VOCs and PAHs	Groundwater	ManTech Environmental POC Ron Adams PE, 703-814-8366

Table 1 Summary of Phase I Survey Sites

Site	Responsible Party	Project Status	Technology and Vendor	Scale	Regulatory Authority	Contaminants of Concern	Media	Point of Contact
Garage Facility, Branchburg, NJ	Municipal Garage Tank Pit	Pilot Completed	Hydrogen Peroxide CleanOx	Pilot Scale	Former UST site cleanup	BTEX	Groundwater	ManTech Environmental POC Ron Adams PE, 703-814-8366
Gas Station, Maxton, NC	Private Site	Pilot Completed	Hydrogen Peroxide CleanOx	Hot Spot Cleanup	Former UST site cleanup	BTEX	Groundwater	ManTech Environmental POC Ron Adams PE, 703-814-8366
Gas Station, Northfield, NJ	Private Site Active Gas Station	Pilot Completed	Hydrogen Peroxide CleanOx	Pilot Scale	Leaking UST	BTEX	Groundwater	ManTech Environmental POC Ron Adams PE, 703-814-8366
Landfill Site, Elizabeth, NJ	Private Site	Pilot Completed	Hydrogen Peroxide CleanOx	Pilot Scale	Landfill contaminated with PCBs	PCBs and PCHs	Groundwater	ManTech Environmental POC Ron Adams PE, 703-814-8366
Fort Stewart, GA	DOD Base Contract	Proposed Project	Hydrogen Peroxide Geo-Cleanse	Pilot Scale	Unknown	Petroleum	Unknown	Geo-Cleanse POC Matt Dingsens 908-686-5959
Chemical Manufacturing Plant, NJ	Private Site	Project Completed	Hydrogen Peroxide Geo-Cleanse	Pilot Scale	Unknown	DNAPL	Unknown	Geo-Cleanse POC Matt Dingsens 908-686-5959
Truck Stop, NJ	Private Site	Project Complete	Hydrogen Peroxide Geo-Cleanse	Pilot Scale	State UST	BTEX	Groundwater and soil	Geo-Cleanse POC Matt Dingsens 908-686-5959
Warehouse	Private Site	Project Complete	Hydrogen Peroxide Geo-Cleanse	Pilot Scale	State UST	Fuel Oil	Groundwater and soil	Geo-Cleanse POC, Matt Dingsens 908-686-5959
11 Gas Station sites in NJ	All are Private Site	1 is closed, 10 awaiting No Further Action from State	Hydrogen Peroxide Geo-Cleanse	Pilot Scale	State UST	BTEX	Groundwater and soil	Geo-Cleanse POC, Matt Dingsens 908-686-5959
US Army Reserve Center, Fort Mill, OH	DOD Base Contract	Proposed Project	Hydrogen Peroxide Geo-Cleanse	Pilot Scale	Unknown	Unknown	Unknown	Geo-Cleanse POC Matt Dingsens 908-686-5959

Characteristics of Phase I Sites
Table 2

Characteristic	DOD ¹	DOE	Private	Total
Number of Sites	14	3	25	42
Contaminants				
CVOC	6	3	10	19
BTEX/TPH	5	--	16	21
Both	1	--	--	1
Unknown	1	--	--	1
Media Treated				
Soil Only	0	0	0	0
Groundwater	2	0	17	19
Both	10	3	7	20
Unknown	2	--	1	3
Oxidant				
Hydrogen Peroxide	12	1	24	37
Potassium Permanganate	1	2	1	4
Ozone	1	0	0	1
Vendor				
GeoCleanse	8	1	4	13
Clean-Ox	3	0	13	16
ISOTEC	1	0	7	8
Other	2	2	1	5
Scale				
Pilot/Demo Only	9	3	15	27
Full Only	1	0	4	5
Both	4	0	6	10
Outcome²				
Success	5	3	11	19
Failure	6	0	0	6
Uncertain	3	0	14	17

¹ DOD Breakdown: Navy (NFESC) = 5; Army(COE)/AF = 7; Army (Base Contract) = 2

² Outcome determinations are relative terms based on available Phase 1 information provided by facility representative (e.g., direct comments or pilot-scale tests that led to full-scale operations). These terms denote the ISO technology's ability or lack thereof to satisfy facility specific program performance objectives.

This information raises considerable concern that ISO has been tried at inappropriate sites, or that the design and/or operation of the system was flawed. Adoption of a new technology can be seriously inhibited by overselling or poor implementation at early sites, and it appears there is a real danger that this is occurring with ISO. It seems clear that better technology selection criteria and guidance on ISO design and operations are needed.

4.2 Phase II Detailed Site Profiles and Results

From the Phase I Site Survey, 10 ISO sites were identified for further evaluation. All these sites were government facilities: 8 were DOD sites, and 2 were DOE facilities. During the review, two additional sites were identified for further evaluation: one was a DOE site and the other was a private site. A list of these sites is shown in Table 3. For each of these sites, more detailed project information was obtained and detailed site profiles were developed.³⁻³⁸

4.2.1 ISO Implementation

Given the potentially large costs and slow pace of cleanups across the country, momentum is gathering for a new site remediation paradigm. The most promising technologies for remediating soil and groundwater are those that treat contaminants in place. The Phase II sites reviewed as part of this study are sponsoring remediation programs involving ISO treatment with the intent of making cleanup objectives more realistic. Key elements of this paradigm being implemented at these sites include the following:

- Increased focus on the development of site-specific risk-based cleanup levels
- Emphasis on source removal, “hot spot” remediation, and containment of lower concentration residuals
- Flexible risk protection goals consistent with future site use; and
- Promotion of less costly innovative remediation technologies, most notably, in situ oxidation.

4.2.2 Site Results

Remediation specialists no longer attempt to fit a site to a standard solution; rather, engineers and scientists use predictive models and treatability tests to determine which technologies are most appropriate for a given situation. Key program objectives, rationales, test results and/or site conditions led to selection of in situ oxidation at the study sites. The strategic remediation approach as well as conditions and results experienced at selected Phase II sites are summarized below.

- A Feasibility Study completed by CRREL concluded that aqueous-phase contamination in ground water may have sufficient potential for self-cleansing and that a pilot test of an in situ air sparging/soil vapor extraction system was inappropriate for remediating groundwater based on modeling and the results of a helium tracer study and neutron logging. The primary remediation issue was determined to be vadose zone soils where

high concentrations of TCE indicated the presence of immiscible-phase TCE. Air-based remediation methods were deemed to be of limited utility due to the concentration of TCE in low permeability units with restrictive capillary effects. Excavation of source material was deemed unfeasible due to the presence of buildings and underground utilities. Injection of an aqueous solution of potassium permanganate to support in situ oxidation and destruction of TCE was the recommended technology. The success of the program is currently inconclusive.

- At the Naval Submarine Base at Kings Bay, Georgia, the Naval Facilities Southern Division recommended the use of in situ chemical oxidation with hydrogen peroxide for source reduction that was based on recent tests at the DOE's SRS. The natural attenuation capacity of the aquifer is expected to polish residuals outside the source area that are less than 100 ppb. Using a predictive model, the NSB's groundwater model determined that the plume would collapse in 5 years. Based on the success of ISO at the site the Georgia Department of Environmental Protection rescinded the consent order and allowed the shutdown of the pump and treat system. In situ oxidation was able to eliminate several DNAPL hot spots and reduce total VOCs in the primary treatment zone to below 100 ppb. The success of this project may be linked to the sandy soil with high hydraulic conductivities (30 ft/day) which makes this an ideal site for ISO implementation. However, the identification of additional source areas following both Phase 1 and Phase 2 treatment gives the impression that the site was not adequately characterized. This raises the challenge of characterizing DNAPL impact below a landfill with the objective of determining the actual amount of DNAPL present and the level-of-effort necessary to complete the remediation.
- In an effort to seek an alternative from pump-and-treat remediation, the Naval Air Station at Pensacola, Florida employed in situ oxidation for source control. As part of a phased approach, the pump and treat operation was first discontinued to evaluate anaerobic conditions that might support natural attenuation. Subsequently, following ISO implementation, good treatment was determined to have occurred in some spots; however, oxidation as part of the Phase I injection project had not significantly reduced contaminant concentrations in the treatment zone. Catalyst chemistry adjustments were then made with the objective of increasing both oxidant/DNAPL contact time as well as the ROI. During the second treatment phase, 60,000 lbs of hydrogen peroxide solution and catalysts were injected. Groundwater results after Phase 2 indicate that in situ oxidation was successful in remediating chlorinated organics found in the treatment zone. However, the site experienced rebound after Phase I. A phased evaluation of natural attenuation as a polishing technology is currently being performed. The evaluation shows that groundwater is approaching clean up standards 200-300 feet from source; therefore, natural attenuation looks promising.
- LEAD was conducting a time critical emergency removal action to remediate a former Oil Burn Pit that, if excavated, would be classified as a RCRA listed F-waste. LEAD selected in situ oxidation because of its combination of low cost and short implementation schedule. The remediation was conducted in two phases. The greatest reductions were observed in the higher VOC concentrations found in the vadose zone. Lesser reductions were observed in the lower VOC concentrations found in the

intermediate and deep zones. However, the system did not meet the objectives of reducing soil concentrations to below the PADEP Act 2 cleanup criteria (<7.2 mg/kg of TCA). It is believed that injection method/rate and placement of wells during Phase I led to insufficient contact of H₂O₂ with the VOCs in the shallow zone. Nonetheless, in light of the remaining low-level TCA concentrations, LEAD believes that may be able to close the site without further aggressive remedial activities and has chosen to evaluate lower cost, follow-up actions to meet the clean up objectives, including enhanced biological treatment, soil vapor extraction, hot spot excavation, and natural attenuation.

- A field demonstration of in situ oxidation through addition of potassium permanganate using DSM was conducted at the DOE Kansas City facility; funding was provided by DOE's Office of Environmental Management (EM-40). Introduction of potassium permanganate oxidant to the subsurface through the DSM process was limited by the low permeability of subsurface soils. Ponding of reagent solution occurred when the soil moisture capacity was exceeded in the shallow treatment cell, resulting in a reduced oxidant loading rate. The technique which uses a crane-mounted vertical mixing blade would not be feasible where foundations or underground utilities are a concern. The persistence of unreacted permanganate in the subsurface would be a concern in soils with a low soil organic matter content and volatilization of VOCs in the off-gas during soil mixing needs to be managed.
- In situ oxidation through injection of a permanganate solution was proposed as an alternative to vapor extraction and groundwater recovery at the BMC Olen site in Irvine, California. In situ oxidation has been considered "successful" in achieving the objective of turning off active remediation systems. The presence of methylene chloride has prevented closure without long-term monitoring to ensure natural attenuation will be effective. In many of the wells, continued injections of permanganate were not possible because of refusal (i.e., the oxidant was forced to the surface during injection). Evidence from injection wells in the center of the plume that could not be reinjected suggests permanganate persisted for an average of 2.5 months, after which, dissolved TCE concentrations rapidly rebounded to approximately half the original concentrations.

4.2.3 Costs

The primary costs associated with implementing an in situ oxidation system include subsurface characterization, development of a geologic conceptual model, design and installation of an effective oxidant delivery system (e.g., soil mixing, injection wells), mass of DNAPL to be remediated, and amount of reagent. The costs associated with in situ oxidation at the study sites were varied or undetermined. Selected cost information at Phase II sites is provided below.

- **Anniston** - The cost data is being evaluated for the project; however, the remediation team believes that the cost of in situ chemical oxidation will be 25% of the cost for excavation and disposal of contaminated soils.
- **Letterkenny (Vadose Zone Soils)** - Actual remediation costs (\$700,000) exceeded the costs projected (\$225,000), but were still significantly less than the projected excavation/treatment/disposal costs (\$3.8M). However, additional treatment must be

performed to meet the cleanup objectives. Based on a what is believed to be a proven design, the contractor believes that bench-scale testing can be reduced or eliminated and remediation costs can be reduced to approximately \$120/lb of total VOCs and \$195/lb of TCE.

- **Savannah River** - The total cost for the pilot test including Site preparation, Pre-test drilling and characterization, Technology test, Post-test drilling and characterization, Post-test demobilization, Documentation, and Project Management was \$511,115. This translates to a unit cost of \$900/lb of DNAPL destroyed for the 600 pounds of DNAPL in the test zone. Unit costs for in situ oxidation based on the pilot test (\$900/lb of DNAPL) are significantly higher than the unit costs for the existing pump and treat system until at the site (\$87/lb of DNAPL). However, due to the program's contractual format requirements, these costs may be higher than ISO costs incurred at other sites. Nonetheless, ISO appears to become competitive when treating 6,500 – 9,500 lbs of DNAPL or more. Additional unit costs were estimated for other DNAPL quantities at that depth:
 - 1,000 lbs - \$469/lb
 - 5,000 lbs - \$126/lb
 - 10,000 lbs - \$83/lb
 - 12,000 lbs - \$73/lb
- **Shaw AFB** - The estimated cost to treat the 400 ft by 300 ft area to 1,000 ppb using 60 injectors was \$2.5M over three years (e.g., based on the pilot test costs and adjusted chemical requirements). The costs did not account for a venting system or additional potential increases in chemical requirements over a larger treatment area. The unit cost for the pilot test of \$8,700 per lb of VOC removed is very high, but it may decrease on a full size remediation project. Compared to the estimated total cost for air stripping (\$540,000) and unit costs for other similar projects, in situ oxidation may have no cost or schedule advantages at this site.

A summary of key site profile information including site specific conditions and process specific data are provided in the following tables:

- Table 4 Soil Parameters at Phase II Sites
- Table 5A Summary of Groundwater Hydrogeologic Data at Phase II Sites
- Table 5B Summary of Groundwater Chemical Data at Phase II Sites
- Table 6 Summary of Design Parameters
- Table 7 Summary of Performance Data

Table 3 Summary of Phase II Sites

Site Location	Area of Concern	Contaminants of Concern	Regulatory Driver	Oxidant	Scale	Remedial Objectives	Ability to Meet Objectives	Follow-up Actions
Anniston Army Depot, Calhoun County, AL	SWMU 12 soils in the former industrial lagoon area	VOCs in soil, primarily TCE	RCRA Corrective Action – Emergency Removal Action	Hydrogen peroxide	Pilot and Full Scale	Reduce chemical contamination that may be contributing to exceedances of health-based concentration limits in onsite and offsite groundwater	Reports claim up to 90 percent removal of total VOCs. Post-treatment sampling data show several areas above the 41 ppm TCE soil cleanup criteria.	Additional polishing treatment in selected locations.
Cherry Point UST Bogue, Carteret County, NC	Vadose zone soils and groundwater in former UST area.	Gasoline and Diesel range organics in soil. VOCs in groundwater, primarily benzene	NCDENR environmental regulations and site cleanup criteria.	Hydrogen peroxide	Pilot Scale	Demonstration project to remediate soil and groundwater within the 1,000 ug/l benzene contour interval to levels acceptable to the NCDENR.	Project caused pavement upheaval, underground explosions, and fire. Post – incident sampling indicates that significant contamination still remains that will most likely require further site characterization and remediation by other means.	Additional site characterization and remediation alternatives will have to be evaluated.
CRREL, Grafton County, NH	AOC 2 (Former TCE UST) & 9 (Ice Well) Vadose Zone Soils	TCE and MEK in soil.	Voluntary clean up. NHDES is the primary oversight agency.	Potassium permanganate	Pilot and Full Scale	Reduce soil concentrations of TCE in vadose zone source area.	Pilot-scale testing is currently inconclusive. Increase of chloride concentrations in pore water during injection provide evidence that the dechlorination reaction is occurring, although pre-and post-injection soil samples indicate limited effect.	Full-scale trial is currently in operation.
Kings Bay NSB, Camden County, GA	Site 11- Former sanitary landfill along the western boundary of the NSB with contaminant plume moving towards residential area.	VOCs in soil, primarily PCE.	RCRA cleanup under a GDEP consent order.	Hydrogen peroxide	Full Scale	Aggressive source reduction with chemical oxidation to 100 ppb VOCs in source area.	In situ oxidation was able to reduce total VOCs in the primary treatment zone to below 100 ppb. The success of this project may be linked to the sandy soil with high hydraulic conductivities (30 ft/day). GDEP rescinded the consent order and allowed the shutdown of the pump & treat system.	Natural attenuation to polish residuals outside the source area that are less than 100 ppb.
LEAD, Franklin County, PA	OBP Vadose Zone Soils	VOCs in soil, primarily TCA.	The OBP is located within a NPL site at LEAD. Working under an IAG with USEPA/ PADEP.	Hydrogen peroxide	Full Scale	Reduce soil concentrations of select VOCs below Act 2 Soil Cleanup Criteria for Groundwater.	In situ oxidation provided significant removals of contaminants. However, in situ oxidation did not meet clean up objectives and additional alternatives will have to be evaluated to achieve greater reductions.	LEAD evaluating: Enhanced biological treatment; Soil vapor extraction; Hot spot excavation; and Natural attenuation.

Table 3 Summary of Phase II Sites

Site Location	Area of Concern	Contaminants of Concern	Regulatory Driver	Oxidant	Scale	Remedial Objectives	Ability to Meet Objectives	Follow-up Actions
LEAD, Franklin County, PA	SE DA Bedrock Aquifer	VOCs in groundwater, primarily TCE.	The entire SE Area including the DA is an NPL site.	Hydrogen peroxide	Pilot Scale	Evaluate Pilot Test results to determine whether ISO alone or combined with other technologies can be used for full-scale remediation.	Not Available	Not Available
Nellis AFB Northeast of Las Vegas, NV	Site ST-44 along the flight line with a plume of TCE impacted groundwater.	TCE in saturated soils and groundwater.	Environmental investigations undertaken through the IRP and overseen by the Nevada DEP. Must comply with Nevada ARARs.	Ozone sparging	Pilot Scale	Determine the feasibility of using in situ ozone sparging to reduce TCE contamination at ST-44.	While in situ ozone sparging appeared to be able to reduce TCE contamination at ST-44 by varying amounts in some wells and spargers, there were increases in other wells and rebound was seen in 4 out of 5 wells and 1 out of 3 spargers.	Full scale treatment with system modifications.
Pensacola NAS, Pensacola, FL	Former Sludge Drying Beds were open surface impoundments that accepted paint wastes and listed hazardous waste.	VOCs in groundwater, primarily TCE.	State order based on monitoring data showing an impact to groundwater. RCRA regulated soils were removed to groundwater and a groundwater pump & treat system was installed.	Hydrogen peroxide	Full Scale	To significantly reduce contamination in the aquifer.	Groundwater results after Phase 2 indicate that in situ oxidation was successful in remediating chlorinated organics found in the treatment zone. However, the site experience rebound after Phase I and the Project Manager expects it again after Phase 2.	Performing a phased evaluation of natural attenuation as a polishing technology.
Shaw AFB, Sumter, SC	OU 4 – Former Fire Training Area No. 1. Soil and groundwater contaminated from the use of combustible liquids in the fire training exercises.	VOCs in soil and groundwater, primarily TCA and DCA.	Site under an ACO. Pilot test performed under TERC.	Hydrogen peroxide	Pilot Scale	- Determine if groundwater contamination at OU-4 can be treated and significantly reduced using hydrogen peroxide solution. - Define the radius of influence of an injection well. - Gather sufficient data to support the design of a full-scale remediation system.	- The pilot test showed that groundwater can be treated to some extent using in situ oxidation; however, it remains to be seen whether significant reductions can be achieved. - The pilot test further defined the radius of influence of an injection well at the site based on the interpolation of several different field measurements. - The pilot test data allowed contractors to adjust the chemical requirements, further define the	The draft Pilot Test Report recommended performing an air sparging pilot test using the existing injector and monitoring well system.

Table 3 Summary of Phase II Sites

Site Location	Area of Concern	Contaminants of Concern	Regulatory Driver	Oxidant	Scale	Remedial Objectives	Ability to Meet Objectives	Follow-up Actions
							radius of influence, and estimate an approximate cost for a full-scale remediation. However, more information is required for remediating contaminants in the vadose zone, remediating contaminants in the lower portion of the aquifer, selecting appropriate injection rates for large-scale areas, and controlling releases of VOCs to the air during treatment.	
DOE Kansas City Plant, Kansas City, MO	Former Ponds Site with VOC contamination in vadose and saturated zone soils.	TCE and DCE in soil.	Not Available	Potassium permanganate	Field Demonstration	Evaluate feasibility of degrading VOCs in situ by addition of KMnO_4 using a DSM Process and evaluate impact of KMnO_4 addition to chemical, physical, and biological properties of the soil being treated.	Oxidant introduction through the DSM process resulted in significant reductions of TCE within the vertical profile of the soil columns and homogenization of the treatment region. Average reduction of TCE levels by 67% in the test cells compared favorably with the 70% treatment goal.	Not Discussed
DOE PORTS, Piketon, OH	Former Area X-701B holding pond used for the neutralization and settling of metal-bearing acidic wastewater and solvent contaminated solutions.	TCE in groundwater.	Pond was closed under RCRA closure action. Site agreed to collaborate with ORNL and support ISO field test at Area X-701B.	Potassium permanganate	Full Scale Demonstration	Field-Scale treatability study of ISCOR to evaluate effectiveness in reducing sources of groundwater plumes and minimizing time pump-and-treat facilities are required to be operational.	In situ oxidation via injection of KMnO_4 solution resulted in dramatic removal of TCE from the Gallia aquifer. However, the persistence of TCE in surrounding units will result in recontamination of the Gallia aquifer over time. Groundwater samples collected 12 weeks after the conclusion of the test suggest that the rate of contaminant rebound will be slow, and that the ISCOR test was successful in reducing the overall mass of TCE within the aquifer unit.	Monitor TCE groundwater levels to determine if further action is needed.
DOE Savannah River Site, Aiken, SC	A/M Area	PCE and TCE in vadose zone soils and soils below the water table.	A/M Area RCRA Groundwater Corrective Action – Integrated Demonstration R&D Activities	Hydrogen peroxide	Pilot Scale	Pilot scale demonstration to evaluate the ability of Fenton's Reagent to destroy DNAPL (TCE & PCE) at a field site and assess the efficiency of Fenton's reagent deployed at depth (150 ft).	In situ oxidation provided significant removals of DNAPL found below the groundwater table in the test zone. While in situ oxidation met the pilot test objectives (verify an alternative DNAPL destruction technology), additional remediation technologies would have to be used in conjunction with in situ oxidation to meet typical aquifer	Not Discussed

Table 3 Summary of Phase II Sites

Site Location	Area of Concern	Contaminants of Concern	Regulatory Driver	Oxidant	Scale	Remedial Objectives	Ability to Meet Objectives	Follow-up Actions
							protection standards.	
BMC Olen, Irvine, CA	Site includes an operating plant that covers much of the source area.	TCE, PCE, and MC in vadose zone soils and below the water table.	Regional Water Quality Control Board	Potassium permanganate	Pilot and Full Scale	Phased objectives: 1.Reduce dissolved TCE and MC levels to asymptote. 2.Turn off active remediation (vapor recovery and groundwater extraction) 3. Obtain site closure. 4.Achieve dissolved TVOC levels below 500 ug/L site wide.	The treatment met the most critical goals of: 1) reducing dissolved-phase CVOC levels (estimated at 97% reduction, to low ppb levels in the injection zone), and 2) terminating active remediation by vapor and groundwater recovery. The treatment did not meet the further objectives of : 1) site closure without long-term monitoring (partly due to the unexpected presence of MC), and 2) a site-wide average dissolved TCE concentration of less than 500 ug/L.	Long-term monitoring will be required as part of the Monitored Natural Attenuation strategy for residual contaminants, particularly MC.

Summary of Soil Parameters at Phase II Sites

Table 4

Site	Bulk Density (g/cm ³)	Porosity (%)	Particle Size	Organic Carbon Fraction (%)	Microbial Enumeration	Chlorinated Organics (mg/kg)	Non-Chlorinated Organics (mg/kg)
Anniston	NA	NA	NA	NA	NA	TCE: 69-26,400 Methylene Chloride : NA PCBs: NA	BTEX: NA Pesticides: NA Phthalates: NA
C.R.R.E.L.	1.55-1.91	43.3	Unsaturated overburden - 92.2% fines Escher sediments - gravel & sand w/trace silt Saturated overburden - fine/med. sands Bedrock - competent and unweathered	0.13 -2.21	NC	TCE: 0.017 - 56,000	NC
DOE Kansas City Plant	1.75	NA	NA	3.0-9.0	Aerobic: 10 ² -10 ⁷ /10g soil Anaerobic: 10 ¹ -10 ³ /10g soil	TCE: ND-2,000 1,2-Dichloroethene: NA	NC
L.E.A.D. Oil Burn Pit	1.73 (undisturbed) 2.08 (remolded Standard Proctor)	47.2-64.3 saturation (undisturbed) 35.3-92.9 saturation (remolded Standard Proctor)	Overburden: predominantly silty fine sand with some clay or silty fine sand Upper bedrock: highly weathered and fractured friable sandstone interbedded with layers of highly weathered shale	1.9-2.6	NA	1,1-Dichloroethane: 9.4-890 1,1,1-Trichloroethane: 7.3-10,000 TCE: 0.5-200 PCE: 0.67-2.0	Total VOCs: 86-1,010 ppm (soil gas) Ethylbenzene: 50-860 Toluene: 49-1,100 Total Xylenes: 1,800-5,300
Cherry Point	NA	15-30	Upper levels: sand Lower levels: silt/clay	NC	NC	NC	GRO: >3,900 DRO: >14,000
Irvine, CA	1.8 (estimated)	30	NA	NA	10 ³ -10 ⁵ cells/gdw	TCE: >10 PCE: low levels Methylene Chloride : NA 1,2-Dichloroethene: low levels Vinyl Chloride: low levels TCA: low levels	NC
Kings Bay	NA	NA	Fine sands with silty and/or clayey fine sands and some medium sands	NA	NA	NA	NA
L.E.A.D. SE Disposal Area	NC	NC	NA	NA	NA	TCE: up to 30,000 (area K-1) Chlorinated VOCs: observed soil staining (area K-1)	NC
Nellis AFB	1.45-1.85	NA	NA	TOC: 783-887 mg/kg	NA	TCE: 43 ug/L (cap. fringe) TCE: 160-330 ug/L (sat. zone)	NC
Pensacola	NA	NA	NA	NA	NA	NA	NA
Portsmouth	NA	NA	Minford layer: silt with scattering of fine to very fine sand Gallia layer: silty gravel matrix with 1/4 to 1 in. size gravels Sunbury layer: black, fissile weathered shale	NA	NA	TCE: ND-80.47 (Minford silt) TCE: ND-302.24 (Gallia S&G) TCE: 0.032-1048.2 (Sunbury shale)	NC
Savannah River	1.4-1.7	0.3-0.6 cm ³ of H ₂ O/cm ³	NA	NA	3.5 x 10 ⁵ cells/gdw	TCE: NA PCE: NA 1,1,1-Trichloroethane: NA	NC
Shaw AFB	NA	NA	NA	NA	NA	1,2-Dichloroethene: 0-35 ppb (soil gas) 1,1,1-Trichloroethane: 0-2,300 ppb (soil gas)	NA

NA Data Not Available

NC Not Conducted

Table 5A Summary of Groundwater Hydrogeologic Data at Phase II Sites

SITE	Water Table Depth (bgs)	Hydraulic Conductivity (cm/sec)	Hydraulic Gradient (ft/ft)	Recharge	Perched Groundwater	Groundwater Divide	Shallow GW/ Surface Water Interaction	Vertical Groundwater Interaction
Anniston	30 ft. (can vary as high as 8-14 ft.)	10^{-7} to 10^{-5}	0.04-0.08	NA	NA	NA	Main discharge point is 2.5 miles south (Coldwater Spring)	Semi-confined flow regime from shallow to underlying aquifer
C.R.R.E.L.	120-135 ft.	Lucstrine unit - 10^{-3} to 10^{-5} Esker - 0.148 Bedrock - 10^{-2} to 10^{-5}	Lucstrine unit: 0.003-0.006 Esker: varies Bedrock - not quantified	Pot. induced recharge to Esker unit from Conn. River due to pumping	Individual clay lenses in vadose zone are nearly saturated	East GW flow in western section of site due to production well pumping	Shallow GW in west part of site unaffected by Conn. River	Recharge in center and west sections of site; discharge in eastern section.
DOE Kansas City Plant	NA	NC	NA	NA	NA	NA	NA	NA
L.E.A.D. Oil Burn Pit	20-30 ft.	NA	Shallow GW from SE area flow east and from DA towards Rowe Run	Infiltration through sinks, fractures and other karst features	None	Divide between Potomac River Watershed and Susquehanna River Watershed occurs between PDO area and SE area	Upper bedrock aquifer feeds local springs and streams	Precipitation recharges bedrock aquifer
Cherry Point	<9-13 ft.	2.68×10^{-2}	0.0025-0.001	NA	No	NA	NA	NA
Irvine, CA	10 ft.	10^{-5} (horizontal) 10^{-8} (vertical)	0.008 (horizontal) 1.2 (vertical) GW velocity=0.5 ft/yr.	Upper zone recharged slowly by infiltration through vadose zone.	Contamination restricted to perched aquifer.	NA	NA	NA
Kings Bay	6 ft.	30 ft/day in impacted zone (30-40 ft bgs)	NA	NA	NA	NA	NA	NA
L.E.A.D. SE Disposal Area	20-30 ft.	$<4.1 \times 10^{-4}$	Shallow GW from SE area flow east and from DA towards Rowe Run	Infiltration through sinks, fractures and other karst features	NC	Divide between Potomac River Watershed and Susquehanna River Watershed occurs between PDO area and SE area	Upper bedrock aquifer feeds local springs and streams	Precipitation recharges bedrock aquifer
Nellis AFB	45 ft.	NA	NA	NA	NA	NA	NA	NA
Pensacola	NA	NA	Affected by pump and treat system	NA	NA	NA	NA	NA
Portsmouth	Gallia S&G saturated approx. 24 ft. below Minford/Gallia interface	Gallia: 8.47×10^{-3} to 1.45×10^{-1}	GW flow is from west to east and discharges into Little Beaver Creek	NA	None	NA	Gallia aquifer discharges into Little Beaver Creek. Plume controlled by interceptor trench.	NA
Savannah River	135 ft.	Upper Zone: 0.009-0.012 Tan Clay: 10^{-7} - 10^{-6} Green Clay: 10^{-8} - 10^{-5}	0.005 (horizontal) 0.28 (vertical)	Upper gw zone recharged by infiltration through vadose zone	Interbedded clay layers in vadose zone that may result in perched gw at several locations	NA	NA	NA
Shaw AFB	17 ft.	NA	NA	NA	NA	NA	Possible connection between shallow gw and Booth's Pond and Long Branch Creek	NA

NA Data Not Available

NC Not Conducted

Table 5B Summary of Groundwater Chemical Data at Phase II Sites

SITE	Field Measurements				Chlorinated Organics (ug/L)	Non-Chlorinated Organics (ug/L)	Metals
	pH (s.u.)	Temp. (°C)	D.O. (mg/L)	Ox./Red Potential (mv)			
Anniston	NA	NA	NA	NA	NA	Phenol: NA	Antimony: unfiltered above MCL Cadmium: unfiltered above MCL Chromium: unfiltered above MCL Iron: NA Lead: unfiltered above MCL Manganese: NA Nickel: filtered & unfiltered above MCL Thallium: unfiltered above MCL
C.R.R.E.L.	7.75-7.82	6.8-26.4	1.58-16.8	99.7-275.7	TCE: 1,190-212,000 (Phase I) TCE: 100-200,000 (Phase II) PCE: 1,290-15,200 (Phase I) PCE: 0-18 (Phase II) Methylene Chloride: 3.04-8,820	Methyl Ethyl Ketone: 7.3 Trimethylbenzene: 6,000 TPH: 544,000-1,990,000 (Phase I) TPH: 0-2,000 (Phase II)	Iron: 0.97-79 mg/L Manganese: NA
DOE Kansas City Plant	NA	NA	NA	NA	NC	NC	NC
L.E.A.D. Oil Burn Pit	NC	NC	NC	NC	NC	NC	NC
Cherry Point	5.7-6.8	21-27	0.07-0.85	+5 to -85	NC	Benzene: 76 - >4,500	Iron: NA
Irvine, CA	6.5-7.5	18-24	1.8 (avg.)	NA	TCE: up to 243,000 Methylene Chloride: > MCL	NA	Iron: NA Manganese: 1,500 ug/L
Kings Bay	NA	NA	NA	NA	Total VOCs: 9,074 TCE: 550 PCE : 8,500 cis-1,2-Dichloroethene: 24	Total VOCs: 9,074	Iron: NA Manganese: NA
L.E.A.D. SE Disposal Area	6.15	NA	NA	NA	Total Chlorinated VOCs: 114,689 TCE: 63,000 1,2-Dichloroethene: 33,000 PCE: 13,000	Total VOCs: 115,262	Iron: 34 mg/L Manganese: NA
Nellis AFB	NA	NA	1.8-3.5	NA	TCE: 2.1-5,000	NC	Iron: 7.3 mg/L Manganese: NA
Pensacola	NA	NA	NA	NA	TCE: 743-2,440 cis-1,2-Dichloroethene: 169-403 Vinyl Chloride: 49.2-976 Chlorobenzene: 2-140	NC	Iron: NA Manganese: NA
Portsmouth	3.0-9.5	12-28	NA	NA	TCE: 50,000-350,000	NC	Iron: NA; Manganese: NA
Savannah River	5.28-9.26	19.2	9.3	NA	TCE: 21.31 (avg.) PCE: 119.49 (avg.) 1,1,1-Trichloroethane: NA	NC	Iron: NA Manganese: NA
Shaw AFB	5.34	NA	2.7 ppm	3-foot thick zone below water table is highly reducing	Vinyl Chloride: 0-455 Chloroethene: 0-3,090 1,1-Dichloroethene: 0-1,850 1,1-Dichloroethane: 0-21,000 1,1,1-Trichloroethane: 0-43,800 TCE: 0-1,160 1,1,2-Trichloroethane: 0-18.3 Tetrachloroethane: 0-48.8 Chlorobenzene: 0-17.9 cis-1,2-Dichloroethene: 0-6,910 1,3-Dichlorobenzene: 0-16.7 1,4-Dichlorobenzene: 0-78.1 1,2-Dichlorobenzene: 0-141	Total VOCs: 0-62,166 Benzene: 0-232 Toluene: 0-3,950 Ethylbenzene: 0-327 Total Xylenes: 0-1,640 Carbon Disulfide: 0-102	Iron: NA Manganese: NA

NA Data Not Available

NC Not Conducted

Table 6 Summary of Design Parameters

Site/ Project Scale	Duration	Affected Area		Soil Volume Treated (yd³)	Contaminant Mass (lbs.)	Injection Wells			Radius of Influence		Oxidation Chemicals				Additional Design Features
	(days)	Surface Area	Depth			No.	(ft bgs)	Screen Length (ft)	Design (ft)	Observed (ft)	Oxidant/ Catalyst	Conc.	Volume (gallons)		
		(ft²)	(ft bgs)										Design	Actual	
Anniston - Pilot Scale	18	3,300	8 to 60	—	—	4	10	2	10	NA	Hydrogen Peroxide/ Ferrous Sulfate	50%¹	NA	7,968	VFB system used to maintain an effective radial dispersion of catalyst and peroxide and to control vent off-gases. Injection of oxidant at 0.25 gpm and 1-5 psi
Anniston - Full Scale Remediation	155	45,000	8 to 27	40,000	71,000	124	15	6	10 to 20	NA	Hydrogen Peroxide/ Ferrous Sulfate	50%¹	NA	132,925	
						68	21	6							
						60	27	6							
C.R.R.E.L. - Pilot Scale	74	NA	NA	NA	NA	2	21	1.5 m	NA	NA	Potassium Permanganate	1.5%	NA	558 g	Injection of oxidant at 0.6-12 psi
Full-Scale Trial	NA	920 m²	3.6 to 9 m	5,300 m³	NA	16	20.5	1.5 m	NA	NA	Potassium Permanganate	1.5%	NA	NA	Automated batch mixing plant with capacity of making 20,000 liters of 1.5% potassium permanganate. Injection of oxidant at 5.3-8.3 l/min and 70 kPa.
DOE Kansas City Plant - Field Demonstration Deep Soil Mixing	NA	NA	NA	NA	NA	—	—	—	8	8	Potassium Permanganate	5.0%	NA	NA	DSM process involved mixing and injection of oxidant solution within 8-foot diameter soil columns using a crane mounted vertical mixing blade. Oxidants were introduced through orifices in the mixing blade. Air was injected during the initial mixing pass to break up the cohesive clay soil and increase permeability for oxidant injection. Testing was conducted in two test cells. Unsaturated soils were mixed to a depth of 25 feet in the shallow test cell, and both saturated and unsaturated soils were mixed to a depth of 47 feet in the deep test cell. Each test cell consisted of three soil columns
L.E.A.D. Oil Burn Pit - Full Scale	35			3,200 tons	5,037	3	8	4	NA	NA	Hydrogen Peroxide/ Ferrous Sulfate	50%¹	8,000	24,000	The remediation was conducted in two phases. Phase I consisted of 14 injector points at 11 locations. Injectors installed at deep, intermediate, and shallow intervals within the OBP and along the perimeter. Three dual injector ports contain shallow and deep injectors. Injected 8,000 gallons of hydrogen peroxide and approximately 7,500 gallons of 300 ppm ferrous sulfate solution over 2 weeks. Minimal injection in shallow zone. Attempted mounding in intermediate zone. Used vfb system part-time. The vfb system consisted of six vacuum hoses that could be connected to any of the injectors at the site. The hoses were connected to a manifold that directed flow through a knockout drum, to remove moisture before reaching the vacuum, and a carbon filter before discharging to air. Phase II included 5 new injectors/vents after bench scale test. Added a soil/cement cap. Doubled the volume of peroxide and the injection time (16,000 gallons of H2O2 over 5 weeks). Ramped the injections and used the vfb system full-time.
						5	14	4							
						6	22	4							
Cherry Point - Pilot Scale	2	NA	NA	NA	NA	4	9-13	NA	NA	NA	Hydrogen Peroxide/ Ferrous Sulfate	50%¹	NA	NA	Pilot test stopped because of explosion and fire.
Irvine, CA - Pilot Scale		5,000	12-16	1,100	800	7	10-12		10	19	Potassium Permanganate	5.1%	2,500 lbs	20,000 lbs	Building housing operating plant covers much of the source area. Air treatment (carbon canisters) for subsurface vapor recovery system. Two clusters added for a third injection to address hot spots. Injection of oxidant at 2.6 gpm and 135 psi.
						7	12-14								
						7	14-16								

---- Not Applicable

NA Data Not Available

¹ Hydrogen peroxide strength prior to dilution and application. Contactor estimated application strength was less than 1% at the injector heads for some sites.

Table 6 Summary of Design Parameters (Continued)

Site/ Project Scale	Duration (days)	Affected Area		Soil Volume Treated (yd ³)	Contaminant Mass (lbs.)	Injection Wells			Radius of Influence		Oxidation Chemicals				Additional Design Features	
		Surface Area (ft ²)	Depth (ft bgs)			No.	Depth (ft bgs)	Screen Length (ft)	Design (ft)	Observed (ft)	Oxidant/ Catalyst	Conc.	Volume (gallons)			
														Design	Actual	
Kings Bay - Full Scale	NA	7,500	30-40	2,778	NA	11 12	29-32 38-42	4 4	NA	NA	Hydrogen Peroxide/ Ferrous Sulfate	50% ¹	NA	12,063		Injection of oxidant at 0.2-1 gpm. Injection of air at 3 cfm.
L.E.A.D. SE Disposal Area - Pilot Scale	12	87,500	70-100	NA	NA	4	70-100	20	50	NA	Hydrogen Peroxide/ Ferrous Sulfate	50% ¹	10,000	NA		A vfb system will be used.
Nellis AFB - Pilot Scale	89	1,080,000	45 and 65	NA	NA	3 3	45 65	NA NA	30-40	100	Ozone	2.5 ppm				Each sparge well consisted of a double screened well with KVA Spargepoints® both within the well and at the bottom of the boring. The C-Sparge™ system is designed to introduce fine bubbles of ozonated air below and into the plume of TCE-impacted groundwater. Within the central part of the well, a submersible pump circulates the water to displace the vertically moving bubbles sideways, increasing dispersion and contact to maximize TCE degradation. A vapor control system (20 cfm) was installed with each Master Unit at the request of the Nevada DEP to account for any VOCs exiting in the off gas from the sparge well. Injection of oxidant at 60 gm/day/well. Injection of air at 20 cfm.
Pensacola - Full Scale	NA	NA	NA	NA	NA	14	NA	NA	NA	NA	Hydrogen Peroxide/ Ferrous Sulfate	NA	95,000 lbs	95,000 lbs		
Portsmouth - Full Scale	NA	10,000	NA	NA	NA	2	220	NA	NA	NA	Potassium Permanganate	1.5% - 2.5%	NA	206,500		The ISCOR test was conducted using a pair of previously installed horizontal wells with innovative filter materials (500 um) instead of conventional screens, located within the area of DNAPL contamination in the Gallia S&G. Groundwater was extracted from the upgradient (west) horizontal well and delivered to the X-623 Groundwater Treatment Facility. Water for oxidant injection was mixed with KMnO4 using a solids feeder. The solids feeder consisted of a hopper and auger system that delivered pre-determined amounts of KMnO4 into a mix tank. The oxidant-dosed water then flowed by gravity into a second mix tank from which a jet pump delivered the oxidant solution to the east horizontal well for injection. Injection of oxidant at 6 gpm.
Savannah River - Pilot Scale	6	2,500	~140	64,000	~593	4	165	5	NA	NA	Hydrogen Peroxide Ferrous Sulfate	50% ¹		7,930 10,000		Four 2-inch injectors, three injectors set in a triangular pattern with the fourth injector located at the center. Overlapping radii of influence. Three monitoring wells located 10 ft out from injectors within the injectors radius of influence. Injection of oxidant at 4 gpm. Three monitoring wells located 10 ft out from injectors within the injectors radius of influence.
Shaw AFB - Pilot Scale	3	120,000	NA	NA	NA	3	23-30	3	25	~30 practical (with 70~ maximum)	Hydrogen Peroxide Ferrous Sulfate	50% ¹	2,000 1,625	2,000 1,625		A nested injector well with two injection points; a shallow injector screened from 20 – 23 feet and a deep injector screened from 27 – 30 feet. The injector well was located 12.5 feet from an existing monitoring well and a new monitoring well. Air was injected at 2 cfm to disperse the reagent solution away from the injector.

--- Not Applicable

NA Data Not Available

1 Hydrogen peroxide strength prior to dilution and application. Contactor estimated application strength was less than 1% at the injector heads for some sites.

Table 7 Summary of Performance Data

Site	Objective	Process Evaluation	Efficiency % Removal	Unit Cost (\$/lb Removed)	Rebound Observed (Yes or No)	Additional Performance Notes
Anniston	Reduce contamination in unsaturated and saturated zones that may be contributing to exceedances of health-based concentration limits in on-site and off-site groundwater.	Approximately 10-20% of injector locations needed additional polishing.	TCE - 73->99%, Total VOC in soils up to 90%	NA	NA	While up to 90% removal of VOCs reported, post-treatment soil sampling data show several areas above TCE soil cleanup criteria.
C.R.R.E.L.	Reduce soil concentrations of TCE in vadose zone source area.	Pilot-scale testing is currently inconclusive; Increased chloride concentrations evidence for dechlorination, although, post-injection soil samples indicated limited effect.	TCE reduction: BAT1 & BAT3 - unremarkable, BAT2 - 70.6%	NA	NA	Results only on pilot-scale demonstration, full-scale trial currently in operation. Detailed stratigraphic data needed for proper injection screen placement and effective delivery. Post-treatment soil sampling method involved separate borings complicating determination of whether TCE concentration changes were due to treatment technology or spacial variability in the soils.
DOE Kansas City Plant	Evaluate feasibility of degrading VOCs and impact to chemical, physical and biological properties of the soil being treated.	TCE removal was within the range of predicted removal rates based on bench-scale tests.	Average VOC reduction - 67%, Individual Test Columns - up to 90%	NA	NA	Introduction of oxidant limited by soil moisture capacity of low permeability soils. Introduction of oxidant did not adversely impact microbial populations, allowing for secondary biological treatment. Use of the DSM process limited to areas with limited subsurface obstructions. Volatilization of VOCs in the off-gas during soil mixing; health and safety concern.
L.E.A.D. Oil Burn Pit	Reduce soil concentrations of select VOCs to PA Act 2 cleanup criteria.	Approximately 17% of soils above cleanup criteria for TCA. High VOC concentrations in shallow zone after Phase I. Remediation dependant on injection method and placement of injection wells. Phase III injection not performed due to Phase II preferential pathways; alternate methods being evaluated.	TCA - 83% of concentrations >7 mg/kg, TVOC - 77% of concentrations >7 mg/kg	Approximate - \$190/lb total VOC, \$287/lb 1,1,1-trichloroethane	NA	Oxidation created off-gases containing VOCs and heated the surface soils; health and safety concern.
Cherry Point	Remediate soil and groundwater within the 1,000 mg/l benzene contour to levels acceptable to NCDENR.	Project caused asphalt upheaval, explosion and fire resulting in cancellation of subsequent phases. Limited remediation in injector area.	NA	NA	NA	Sites with asphalt or concrete should be vented; utility survey needed prior to implementation. Accident caused by unexpected levels of GRO in the upper soil. Site was not adequately characterized to support system implementation.
Irvine, CA	1) Reduce TCE and MC levels to asymptote. 2) Turn off active remediation. 3) Obtain Site Closure. 4) Achieve dissolved TVOC levels below 500 ppb site-wide.	Site-wide concentration of 500 ppb never reached. In many wells refusal stopped continued injection. Initial injection apparently filled flow paths so that much lower volume injected second and third times. ROI of 19 feet exceeded design goal of 10 feet.	No reduction in MC was noted. TCE in dissolved phase reduced in the ZOI by 97% on average.	\$375/lb CVOC, based on upper estimate of 800 lb	Yes	Probably more effective to use new injection points for consecutive injections. Treatment caused near sterilization in the source area, but microbial populations remained in downgradient groundwater. Active remediation discontinued, monitored natural attenuation is being pursued. Permanganate persisted average of 2.5 months after injection; TCE rebounded to ~ 1/2 original levels in most cases and to pre-treatment levels in one case. Based on permanganate consumption, significant amount of DNAPL treated.
Kings Bay	Achieve 100 ppb VOCs in source area; plume degradation prior to reaching compliance point; and plume collapse in 5 years. Goals will be achieved via source reduction with chemical oxidation; pump and treat of intermediate plume for 1 year; and monitored natural attenuation.	TVOC in the primary treatment area dropped from 9,074 ppb to 90 ppb. Previously unidentified upgradient source found at injector outside primary treatment area.	99% reduction in primary treatment area after 2 phases of injection	NA	No	Based on success, GDEP rescinded consent order and allowed shut-down of pump and treat system. Identification of additional source areas raises questions about completeness of site characterization and actual amount of DNAPL remediated. Photographs show wells overflowing, presumably due to pressure gradient caused by oxidation reaction; health and safety concern. No rebound; subsequent results indicate concentrations have remained below 100 ppb.
L.E.A.D. SE Disposal Area	Evaluate the results of the pilot-scale studies to determine whether an individual or combined remedial approach can be used in the full-scale remediation of groundwater.	Pilot test to be performed in the near future, no information to evaluate.	NA	NA	NA	

NA Data Not Available

Table 7 Summary of Performance Data (Continued)

Site	Objective	Process Evaluation	Efficiency % Removal	Unit Cost (\$/lb Removed)	Rebound Observed (Yes or No)	Additional Performance Notes
Nellis AFB	Determine the feasibility of using in situ ozone sparging to reduce TCE contamination.	Groundwater ROI may be greater than sparging ROI. Based on current testing in Europe, vendor believes ROI can be increased to 100 feet or greater using double-screened circulation wells, larger pumps, and pressure relief between layers to encourage contact and recirculation.	Some reduction detected during operation; post-shutdown data indicate significant rebound	NA	Yes	Questionable whether in situ ozone sparging is feasible without more performance data showing greater reductions and some cost data. First phase of operation saw many difficulties including low permeability soils, security problems, and equipment failure. Rebound observed in 4 of 5 wells and 1 of 3 spargers.
Pensacola	To significantly reduce contamination in the aquifer.	Short circuiting occurred during Phase I. More information required to perform a thorough evaluation of the system performance.	~ 95% reduction of chlorinated solvents after Phase II		Yes	USGS evaluating natural attenuation as polishing technology with pump and treat system operating. Evaluation shows groundwater approaching clean up standards 200-300 feet from source. Phase II of USGS evaluation will be performed without pump and treat system. Rebound occurred 16 days after Phase I completed. Expected again after Phase II.
Portsmouth	Field-scale treatability study of ISCOR to evaluate the effectiveness in reducing sources of groundwater plumes and minimizing time pump and treat facilities are required to operate.	System required temporary shutdown due to shutdowns of the pre-treatment system, water backing up in the injection well, heavy rainfall tripping leak detectors, and system repairs. Target injection rate was 10 gpm, but only 6 gpm was possible without water backing up to ground surface (e.g., due to either heavy rainfall or clogging of the screen by undissolved oxidant or precipitates).	Decrease in TCE to ND after passage of oxidant front; TCE concentrations in DNAPL area below 5 ppb MCL after treatment.	NA	Yes	Subsequent modeling indicated superior distribution of oxidant would result from injection through an array of vertical wells. TCE concentrations were sharply reduced in soil and groundwater in areas where oxidant migration occurred. Due to the persistence of TCE in the overlying and underlying fine-grained units, some source material remains to impact future groundwater quality. Extracted water clear initially and became turbid, apparently due to amorphous manganese oxides, end product of reaction. Oxidant migrated to extraction well at the ends leaving "dead-zone" in the central section. Minimal rebound based on groundwater sampling conducted 12 weeks after termination of treatment.
Savannah River	Pilot-scale demonstration to 1) evaluate the ability of Fenton's Reagent to destroy DNAPL (TCE & PCE) at a field site and 2) assess the efficiency of Fenton's Reagent deployed at depth (150ft).	Results during pilot test indicate in situ oxidation successful in remediating DNAPL below water table. Post-test characterization of groundwater showed increase of PCE and TCE concentrations back towards equilibrium in and outside test zone.	94%	\$900/lb for 600lb; cost decreases with increased volume treated	Yes	While in situ oxidation met the pilot test objectives, additional remediation technologies would be required in conjunction to meet typical protection standards. Injection method and aquifer conditions appear to have provided good contact between oxidation agent and DNAPL, but DNAPL that did not contact oxidation agent and DNAPL outside test zone led to rebound. Air sparging and oxidation created off-gases that vented through monitoring wells/injectors; health and safety concern. Rebound occurred due to remaining DNAPL in the test zone and DNAPL present outside of the test zone.
Shaw AFB	Determine if groundwater contamination can be significantly reduced using hydrogen peroxide solution. Define the ROI of an injection well and gather enough data to support the design of a full-scale system.	Post-treatment soil gas sampling showed increased VOCs. Post-treatment groundwater sampling indicated decreased concentrations in all contaminants. Evidence of chemical oxidation: increases in carbon dioxide in soil gas; increases in chloride in groundwater; appearance of acetone in groundwater after treatment. Pre-pilot test ROI estimated at 25 feet, actual average ROI was 30 feet.	~ 50 % for all contaminants except DCE and benzene	\$8,700/lb of VOC, may decrease on a full-scale system	Yes	Disagreement of what mechanism was responsible for contaminant reduction, air stripping or oxidation. In addition, dilution has been identified as partially responsible for the reductions. A strong reducing environment in the treatment zone acted as an oxygen sink, limiting the effectiveness of oxidation. Control of the off-gases required to maintain health and safety. There is no evidence that in situ oxidation can achieve the final remediation goal of 1,000 ppb total VOCs for this site. Rebound occurred from the vadose zone contamination or increased soil gas concentrations.

NA Data Not Available

5 Lessons Learned

Section 5.1 provides the site conditions associated with successful as well as unsuccessful ISO technology implementations. From this data and the results of the Phase II site profiles, specific lessons were learned (Section 5.2) and additional information needs identified (Section 5.3).

5.1 Inferences Regarding the Impact of Site Conditions on the Success of an ISO Implementation

Subsurface characterization and the development of a geological conceptual model that details the stratigraphy and preferred flow pathways (areas of greater transmissivity) are essential to implementing effective in situ oxidation treatment. In addition, there may be limitations both on the delivery of the oxidant as well as its stability in the subsurface. For example, in clay strata the delivery of reagents may be very poor or not possible at all without some modifications to the subsurface. In other instances, the contaminant may be trapped or pooled in rock fissures or cracks or may be bound within the soil matrix. Notable conditions and design features at selected study sites are summarized below.

5.1.1 Conditions Associated With Successful Technology Implementation

- Using extensive soil sampling, the Anniston Army Depot remediation team was able to accurately define the zone and quantity of contamination. Subsequently, the team was able to select appropriate injection well spacing, injection rates and quantities. Key features of their full-scale in situ oxidation program include the following:
 - Installation of over 250 injection wells at three depth intervals to permit introduction of peroxide. Wells set at 10-20 ft intervals based on results of demonstration project.
 - Injection beginning at the upper levels of the impacted area and continuing downward. Injection proceeded at a rate of 0.25 gpm and pressure of 1-5 psi.
 - Use of a vent flow balance (vfb) system to maintain an effective radial dispersion of catalyst and peroxide and control vent off-gases (steam, oxygen, carbon dioxide, and products of reaction).

Over a 5-month period 132,925 gallons of hydrogen peroxide were injected. As part of post-treatment sampling, approximately 10 to 20 percent of the injector locations underwent additional polishing through either existing injectors or new injectors. The removal action reportedly reduced total VOC contamination in soils up to 90%. While reports claim up to 90 percent removal of total VOCs, post-treatment sampling data show several areas above the 41 ppm TCE soil cleanup criterion.

- The CRREL remediation team implemented injection of an aqueous solution of potassium permanganate to support in situ oxidation and destruction of TCE. The

perceived benefits of aqueous permanganate delivery include stability of the oxidant relative to hydrogen peroxide, dispersion in the unsaturated zone by gravity induced drainage and capillary pressures that would inhibit gas delivery systems into low-permeability units, and ability to react under a broad range of pH. The potential adverse effects include generation of carbon dioxide in concentrations above aqueous solubility limits creating a gas phase which would decrease effective porosity, and reduction in porosity due to the precipitation of MnO_2 , a by-product of permanganate reduction. The results of the pilot-scale test were encouraging, although equivocal regarding the overall effectiveness under specific site conditions:

- Vadose zone soils are vertically and horizontally heterogeneous. Delivery of the oxidant solution depended on injection into higher permeability units, followed by dispersion and diffusion into low permeability units where residual TCE was concentrated. This requires detailed stratigraphic data to support proper injection screen placement.
 - Pre-injection and post-injection soil samples were obtained from separate boring locations. The heterogeneity of the vadose zone soils, and the variability of residual TCE concentrations (often ranging over several orders of magnitude) complicate determining whether TCE concentration changes were due to the treatment technology or spatial variability independent of treatment.
 - Pore water samples documented an increase in chloride concentration during oxidation. These results support dechlorination of TCE and provide the strongest evidence for the efficacy of the technology. Variable chloride concentration responses may be due to subsurface flow paths of pore water and relative sensitivity of ceramic versus stainless steel lysimeters.
 - Changes in concentrations of potassium, manganese, and chloride in pre- and post-injection soil samples were unremarkable. Cation exchange coefficient and soil pH exhibited a slight, but consistent increase, consistent with the predicted deposition of MnO_2 .
 - Key questions regarding rate of diffusion into low-permeability units, rate of reaction, rate of dissolution of TCE from residual liquid into aqueous solution in pore water, and potential reduction of effective porosity due to generation of gas phase CO_2 and MnO_2 precipitation are not experimentally evaluated within the pilot test.
- The DSM process at the DOE's Kansas City facility involved mixing and injection of oxidant solution within 8-foot diameter soil columns using a crane mounted vertical mixing blade. Oxidant solution, consisting of 5 wt % potassium permanganate, was introduced through orifices in the mixing blade. Air was injected during the initial mixing pass to break up the cohesive clay soil and increase permeability for oxidant injection. Testing was conducted in two test cells. Unsaturated soils were mixed to a depth of 25 feet in the shallow test cell, and both saturated and unsaturated soils were mixed to a depth of 47 feet in the deep test cell. Each test cell consisted of three soil columns. The introduction of oxidant through the DSM process resulted in significant

reductions of TCE within the vertical profile of the soil columns and homogenization of the treatment region. Average reduction of TCE levels by 67% in the test cells compared favorably with the 70% treatment goal. Oxidant loading rates in the field demonstration were 60% lower than oxidant loading rates evaluated during the bench-scale testing due to the limited moisture capacity of the treated soils, which limited the volume of reagent injected during the mixing process.

- The Naval Submarine Base at Kings Bay Georgia utilized hydrogen peroxide as an in situ oxidation means toward source remediation. During the initial injection (Phase 1), 8,257 gallons of hydrogen peroxide (50% solution) and similar amounts of ferrous sulfate catalysts were injected from 0.2 to 1.0 gpm. Air was injected at 3 cfm to disperse the catalysts. Variable volumes of hydrogen peroxide were injected into the wells based on contaminant mass loading within the treatment area. An additional injection (Phase 2) was performed using 3,806 gallons of hydrogen peroxide (50% solution) and similar amounts of ferrous sulfate catalysts. At the completion of treatment, total VOCs in the primary treatment area had dropped from 9,074 µg/l to 90 µg/l for a 99 percent reduction. Groundwater results at the conclusion of injection indicated that in situ oxidation was successful in remediating DNAPL to below 100 ppb in the primary treatment zone. Subsequent results have shown that concentrations remain below 100 ppb. Groundwater results outside the primary treatment zone indicate the existence of other source areas outside the primary treatment zone.
- Although the Phase II remediation had not achieved the clean up objectives, LEAD determined that a Phase III injection was not feasible because of the creation of preferential pathways along the vents and slight differences between onsite soil types (e.g., sandy loam vs. silt loam and silty clay loam). Preferential pathways can be created during the oxidation process as off-gas pressure generated by the chemical oxidation process vents at the ground surface producing steam and at times liquid flow. During liquid flow, silts and clays are transported to the surface creating voids along the vent pathways. These voids can cause short-circuiting by stopping the injected fluids from reaching the contaminated area or reducing the contact time with the contaminate soil. Short-circuiting can also occur when injecting into non-homogeneous soils that have layers with different permeabilities. The preferential pathways that developed were confirmed during post-injection confirmation sampling. The Geoprobe™ macrosampler dropped 1 to 2 feet when these voids were encountered beneath the soil-cement cap. These pathways would make it difficult for further injections of H₂O₂ to reach the remaining contamination.
- Groundwater results during the Savannah River facility pilot test indicated that in situ oxidation was successful in remediating DNAPL found below the groundwater table in the test zone. At the completion of the pilot test, PCE and TCE concentrations in groundwater had been reduced three orders of magnitude and chloride ion concentrations were eight times higher indicating the oxidation of PCE and TCE. In addition, post-characterization soil results (94 % reduction) confirm that in situ oxidation was successful in remediating DNAPL found below the groundwater table in the test zone. While in situ oxidation met the pilot test objectives (verify an alternative DNAPL

destruction technology), additional remediation technologies would have to be used to meet typical aquifer protection standards.

5.1.2 Conditions Associated With Unsuccessful Technology Implementation

- Under the Navy's RAC, MCAS Cherry Point was remediating a former UST area. Based on available information, an ISO treatment program was designed wherein the first phase consisted of four injectors releasing oxidation agents (hydrogen peroxide, ferrous sulfate catalyst, and phosphoric acid) to shallow groundwater at elevations 9-13 feet bgs. On the second day of the demonstration project, the in situ oxidation project caused pavement upheaval, underground explosions, and fire. As a result, subsequent project phases have been canceled. The pavement heaving, small explosions, and fire were caused by unexpected levels of gasoline range organics in the upper soil. The organics reacted with hydrogen peroxide resulting in excessive heat and off-gassing pressure sufficient to uplift the asphalt pavement and fill existing voids around an abandoned sewer pipe. Heat, oxygen, and petroleum constituents then combined to produce the explosions and fire. The site was not adequately characterized to safely support implementation of the hydrogen peroxide. The resultant implementation strategy was flawed for this particular site because of, but not limited to the following:
 - The injection wells delivered oxidation chemicals into shallow groundwater (9 ft bgs) when unidentified, significant contamination existed just below the surface. At sites where elevated contaminant levels are identified, a "top down" injection approach used successfully at other sites would have created a blanket to consume organics as they rise.
 - There was no venting or negative pressure system to accommodate off-gasses and relieve pressure and build up of organics under the pavement.
 - No accommodation was made for the potential of abandoned piping found at the site to create preferential pathways and/or pockets for organic decomposition, explosive liquids and vapors, and oxygen. Comprehensive and credible utility surveys should be done well in advance of field implementation so that below ground obstacles, pipelines, and trenches can be identified and accommodated in the design.
 - No monitoring was performed in the upper soil zone to effectively identify a potential runaway reaction event. Contingency procedures must include priority emergency actions to stop or slow the reaction. No specific contingencies were made in the Health and Safety Plan for below ground explosions.
- The C-Sparge™ system used at Nellis AFB is designed to introduce fine bubbles of ozonated air below and into the plume of TCE-impacted groundwater. Within the central part of the well, a submersible pump circulates the water to displace the vertically moving bubbles sideways, increasing dispersion and contact to maximize TCE degradation. Based on pre-pilot testing, the ROI was estimated at approximately 30 to 40 feet. The air/ozone mixture was set and maintained at 2.5 ppm ozone concentration for a total loading of 60 grams ozone per day from each master unit. A vapor control system

(20 cfm) was installed with each Master Unit at the request of the Nevada DEP to account for any VOCs exiting in the off gas from the sparge well. The first phase of the test saw many difficulties with the pilot system due to low permeability of soils. In addition, there were electrical supply difficulties and interference/system shutdown by unknown personnel. Difficulties with well packer assemblies resulted in blowouts under system pressures and dead heading of pumps. In situ ozone sparging appeared to be able to reduce TCE contamination in some wells and spargers; however, rebound was seen in 4 out of 5 wells and 1 out of 3 spargers.

- As part of the field test conducted at the DOE's Portsmouth Gaseous Diffusion Plant in Piketon, Ohio, extracted groundwater was dosed with KMnO_4 to yield a 1.5% -2.5% solution and reinjected into the aquifer to oxidize dissolved phase TCE and reduce DNAPL mass within the aquifer. Movement of the permanganate front throughout the test revealed the degree of non-uniform flow between the recirculation wells. The oxidant migrated toward the extraction wells along two preferential lobes at either end of the injection well with a sizeable "dead-zone" apparent in the central section. Oxidant was distributed within the central section of the treatment area only after vertical injection was initiated through a selected monitoring well during the latter stages of the test. The results of subsequent (though unreported) modeling indicated that superior distribution of oxidant within the aquifer would result from injection through an array of vertical wells. Where the oxidant was demonstrated to permeate the aquifer, significant reductions in TCE were measured in both groundwater and soil samples. The appearance of permanganate in the groundwater resulted in an immediate decrease in TCE concentrations to very low to non-detectable levels. Oxidation of TCE appeared to be restricted to the more permeable sand and gravel unit, with little or no impact on TCE levels in soils collected from the overlying silt or the underlying shale. Due to the persistence of TCE within these underlying and overlying fine-grained units, where infiltration of the oxidant was minimal under saturated conditions, some source material still remains to impact future groundwater quality. Distribution of permanganate was also non-uniform between recirculation wells, due to vertical and lateral variation in hydraulic conductivity and possible blockage in the central injection well section well. The recirculation system was designed to run continuously throughout the test duration. The target injection rate was 10 gpm; however, the injection well could only inject at a rate of 6 gpm without water backing up to the surface. Water backing up appeared to be due to either heavy rainfall or the well screen clogging due to undissolved oxidant or precipitates. Overall recirculation well flow was relatively steady.
- Groundwater results during the Shaw Air Force Base pilot test indicate that ISO had limited success in treating VOCs in the groundwater of a treatment zone area that proved difficult to define. Furthermore, the concentrations of certain chemicals in groundwater increased within and outside the treatment zone. In addition, a strong reducing environment in the treatment zone is acting as an oxidant sink and appears to be limiting the effectiveness of chemical oxidation.

5.2 Considerations For Technology Implementation

This report is not intended to serve as a guidance document; however, various key factors have been identified from this study that should be considered at other sites where ISO is proposed to remediate DNAPL. These factors are described below under three categories: Site Characterization Needs; Design Issues; and Operational Issues.

5.2.1 Site Characterization Needs

- **Total Oxidant Demand** - Although the stoichiometry of CVOC oxidation is known, non-target materials in the subsurface can exert a considerable additional oxidant demand. Natural organic acids, reduced iron and manganese, and sulfides can all consume oxidant. Data on the concentrations and fluxes of these materials in the treatment zone are essential to rational design, and a simple spreadsheet model should be available to estimate total oxidant demand based on the site characterization data.
- **Contaminant Delineation** - Better methods are needed to delineate the locations and extents of soil contamination and particularly DNAPL accumulations. Without knowledge of upper soil contamination, oxidants can react with organics near the surface and result in excessive heat and off-gases. Without a clear delineation of DNAPL locations, untreated DNAPL from areas outside the treatment zone can serve as a reservoir for continuing groundwater contamination.
- **Mass Estimates** - Contaminant concentrations in groundwater have been used for the design and performance assessments at several of the sites. The results from these sites have included unacceptable rebounds because CVOCs diffused into the groundwater from untreated materials. In most cases, an argument can be made that natural attenuation can provide protection after sufficient mass has been removed, even if rebound occurs, but without direct measurements of the total CVOC mass before and after treatment, such a strategy is difficult to defend.
- **Vapor Monitoring** - The presence of potentially explosive vapors in the subsurface is not always verified at sites where CVOC contamination is known to occur. However, before selecting and using ISO, a soil vapor survey in the area should be completed to prevent possible health and safety hazards during treatment.

5.2.2 Design Issues

- **Radius of Influence** - Better guidance on the expected ROI is needed. At this point, most designs have been based on professional judgement. In the cases where the ROI was measured, the actual ROI has differed significantly from the design basis.
- **Oxidant Concentration** - The concentration of oxidant in the injected water has been different in virtually every case examined. There does not appear to be clear guidance on the concentration that should be used. Apparently, concentrations can be high enough to cause undesirable reactions (such as excessive heat generation or foaming), but clear guidelines on optimal concentrations are not available.

- **Enhance Mixing** - There may be several methods available to enhance mixing and therefore contact between contaminants and oxidants, but clearly this should be a key design objective and it has not always received sufficient attention at the sites studied. Methods used have included multiple injections in the same or different locations, multiple screened intervals at one location, high-pressure injection to induce subsurface fracturing, recirculation, vapor injection/ recovery, and capping. At Letterkenny, for example, these types of enhancements caused significant improvements in Phase 2 as compared to Phase 1.
- **Incorporate ISO Into an Overall Site Management Strategy** – ISO should be viewed as part of the overall approach to remediating DNAPL sites. Vendors agree that ISO is most appropriate for source removal, and other technologies that are more cost effective may be needed for the residual contaminants after treatment. At several sites, ISO was used for source reduction, and some residual material remained. Site managers then decided to use more cost effective approaches after ISO (e.g., natural attenuation or sparging). At most sites, the design and remedial goals should probably be based on a strategy that combines ISO to the extent practicable, followed by techniques more appropriate for dissolved phase contamination and relatively low levels of residual DNAPL.

5.2.3 Operational Issues

- **Consider Multiple Injections** - Even when the initial response seems highly encouraging, reinjection into the same, or preferably new locations, should be considered. Most subsurface environments are highly heterogeneous, and a one-time injection is unlikely to deliver oxidants to all of the impacted areas. Injecting into new injection points can circumvent the problems of the development of preferential flow paths from the original injection points, and the short-circuiting observed at some sites after the first injection due to plugging of the flow paths.
- **Monitor Vapors for VOCs and Explosion Potential** - During drilling and injection, projects should include a formal requirement for vapor monitoring to prevent incidents like that at MCAS Cherry Point. Monitoring for VOC off-gassing can indicate both health and safety concerns as well as indicate the probability of contaminant loss via volatilization.
- **Monitor for Rebound** - The potential for rebound in groundwater concentrations is often not fully appreciated. Rebound does not necessarily mean ISO was a failure. If the emphasis is placed on mass removal as a primary remedial objective, the rate and extent of rebound can help in the design of any needed subsequent remedial steps.

5.3 Additional Information Needs

The results of this study have pointed out the need for better guidance on the selection and use of ISO. Several failures have been reported. In particular, the explosion at MCAS Cherry Point serves as a warning that ISO is a potentially hazardous operation that requires careful health and safety precautions.

Pilot-scale testing of the efficacy of in situ oxidation of TCE is currently inconclusive. Further testing is necessary to bridge the fundamental theories of the laboratory with the needs of the remediation team. The most important issues associated with the goal of integrating in situ oxidation science with solutions to real-world problems include the following:

- the fate and behavior of the oxidant in the subsurface environment; and
- the design features of the technology that ensure effective treatment.

These issues are discussed below.

5.3.1 Fate and Behavior of Oxidant

The fate and behavior of the oxidant being introduced to the subsurface remains undefined. Consequently, the following issues will continue to affect the success of in situ oxidation technology:

- **Verification of Effective Treatment** - The rebound of groundwater concentrations following treatment demonstrates that groundwater measurements are not the most accurate method for defining the NAPL zones during characterization or quantifying the amount of NAPL that was remediated. Although increases of chloride concentrations in pore water during injection provides evidence that the dechlorination reaction is occurring, pre- and post-injection soil samples often indicate limited effect. Soil pore water samples have also been used to document a decrease in TCE concentrations, except where residual TCE may remain. Often, a soil confirmation program is complicated by vertical and horizontal variability in contaminant distribution, with greater variability in contaminant concentration documented in space versus over time.
- **Determination of Treatment Mechanisms** – There continues to be disagreement over in situ oxidation technology monitoring results that exhibit both the reductions in groundwater contaminant levels and increases in soil gas. Three mechanisms have been potentially identified as responsible for contaminant reductions:
 - Chemical oxidation of VOCs;
 - Volatilization, air stripping, and partitioning of VOCs to vapor or gas phase; and
 - Direct dilution of VOCs by injection of uncontaminated liquids.

At Shaw AFB, modeling results and chloride concentrations support air stripping as being largely responsible for initial contaminant reductions during the pilot test. However, it remains unclear whether increases in soil temperature caused by ISO implementation, caused in turn, increases in soil gas concentrations and rebound in the groundwater samples. If the hydrogen peroxide in situ oxidation process is actually reducing contaminant concentrations through volatilization and air stripping, this raises questions regarding the overall efficiency and cost of in situ oxidation versus other technologies (i.e., air stripping, steam stripping, or soil vapor extraction).

- **Delineation of Subsurface Conditions Affecting Technology** – In order to achieve treatment performance objectives, it will be necessary to match the oxidant delivery system based on the target contaminants and the site specific conditions. As noted from this study, the variability of these site specific conditions as they affect technology performance may be most pronounced in the intermediate and deep zones of the subsurface. For example, at Shaw AFB the ROI was initially assumed to be 25 feet. However, based on the concentration of VOCs in shallow soil gas samples, the fraction of VOCs remaining in groundwater, and the changing groundwater temperatures, the actual ROI was estimated to be 70 feet. In addition, the sampling strategy employed at the Savannah River Site exemplifies the concept that sampling several media, other than just groundwater, is necessary to effectively measure the remediation capabilities of in situ oxidation. The subsurface factors most likely to affect in situ oxidation performance include the following:
 - Matrix characteristics
 - Subsurface heterogeneities and their constraint(s) on oxidant delivery systems.
 - Contaminant and process induced effects including gas evolution, development of macropores, generation of precipitates (e.g., MnO_2) and changes in redox potential as affecting the required amounts of oxidant;
 - Pathways and risk associated with untreated residuals, reactants and byproducts.

5.3.2 Design Issues for Field Demonstrations

Since the kinetics of oxidative treatment are extremely fast in comparison to dispersion of the oxidant throughout the treatment area, design issues associated with transport limitations are often the most controlling. Design issues at the study sites include:

- **CRREL** - Decrease of effective porosity due to precipitation of MnO_2 and generation of gas phase CO_2 limiting access to residual TCE in pore space
- **Kings Bay Naval Submarine Base** - A review of photographs shows a well overflowing, presumably from pressure gradients caused by the oxidation reaction. Therefore, it is possible that air sparging and oxidation during injection created off-gases containing VOCs that vented through monitoring wells/injectors. Off-gases create health and safety concerns and required engineered controls.
- **Nellis AFB** – The groundwater ROI may be greater than the sparging ROI. Design modifications being considered include installation of double-screened recirculation wells, implementation of recording piezometers and groundwater flow meters to verify proper circulation, larger pumps, and pressure relief between layers to encourage contact and recirculation.
- **LEAD** - Remediation appeared to be very dependent on the injection method and the placement of injection wells. To note, injection methods/rates created preferential

pathways that isolated areas of contamination and prevented further use of in situ oxidation. In addition, oxidation created off-gases containing VOCs that vented through the surface and heated the surface soils. Controlling venting of the off-gases was necessary to reduce the potential for creating voids and reduce health and safety concerns.

- **Pensacola NAS** - Phase 1 activities experienced inefficient reagent delivery dispersion due to elevated levels of dissolved iron. Subsequent modification of the injection process was necessary to address unanticipated subsurface conditions.
- **DOE Portsmouth** - Improved oxidant distribution in the subsurface is being explored via injection through an array of vertical wells rather than horizontal wells.

Cleaning up subsurface pollution is one of the most formidable challenges in the realm of environmental stewardship. As determined through this study, conventional approaches to subsurface remediation are likely inadequate for achieving regulatory cleanup levels at most sites. A summary of selected contaminant cleanup standards for Phase II site states is provided in Table 8.

Table 8
State Target Levels for Soil
(values in mg/kg)

	ORGANICS												
	PCE	TCE	1,1,1-TCA	1,1-DCE	trans-1,2-DCE	cis-1,2-DCE	DCA	DCM	VC	Chloro-benzene	MEK	Ethyl-benzene	PCB
Alabama	12	58	1600	1.1	1600	780	7800	85	0.34	1600	47000	7800	0.32
California	4.7	2.7	6.8	0.052	620	420	570	8.5	0.02	54	6900	230	0.2
Florida	8.9	6	400	0.09	31	19	290	16	0.03	30	3100	1100	0.5
Georgia	0.18	0.13	0.5	0.36	NG	NG	0.03	0.08	0.04	4.18	0.79	20	NG
Missouri	0.42	0.097	4.67	0.1	1.13	0.51	0.024	0.021	0.016	2.2	NG	55	NA ¹
Nevada	4.7	2.7	6.8	0.052	620	420	570	8.5	0.02	54	6900	230	0.2
New Hampshire	2	0.8	42	1	9	2	3	0.1	0.4	6	2	140	1
Ohio	94	77	1200	410	910	450	620	220	0.58	NG	6600	230	1
Pennsylvania	0.43	0.17	7.2	0.19	2.3	1.6	0.65	0.075	0.027	3.4	53	46	0.52
South Carolina	12	58	1600	1.1	1600	780	7800	85	0.34	1600	47000	7800	0.32

State Target Levels for Groundwater
(values in mg/L)

	ORGANICS												
	PCE	TCE	1,1,1-TCA	1,1-DCE	trans-1,2-DCE	cis-1,2-DCE	DCA	DCM	VC	Chloro-benzene	MEK	Ethyl-benzene	PCB
Alabama	0.0011	0.0016	0.54	0.00004	0.122	0.061	0.8	0.0041	0.000019	0.11	1.9	1.3	0.00003
California	0.005	0.005	0.005	0.006	0.01	0.006	0.005	0.005	0.0005	0.07	NG	0.7	0.0005
Florida	0.003	0.003	0.005	0.007	0.1	0.07	0.07	0.005	0.001	0.1	4.2	0.03	0.00005
Georgia	0.005	0.005	0.005	0.007	0.1	NG	0.005	0.005	0.002	0.1	2	0.7	0.0005
Missouri	0.005	0.005	0.2	0.007	0.1	0.07	0.005	0.005	0.002	0.1	NG	0.32	0.0005
Nevada	0.005	0.005	0.2	0.007	0.1	0.07	0.005	0.005	0.002	0.1	1.9 [a]	0.7 [b]	0.0005
New Hampshire	0.005	0.005	0.2	0.007	0.1	0.07	0.005	0.005	0.002	0.1	0.17	0.7	0.0005
Ohio	0.005	0.005	0.005	0.007	0.1	0.07	0.005	0.005	0.002	NG	8.6	0.7	NG
Pennsylvania	0.005	0.005	0.2	0.007	0.1	0.07	0.005	0.005	0.002	0.1	NG	0.7	0.0005
South Carolina	0.005	0.005	0.2	0.007	0.1	0.07	0.005	0.005	0.002	0.1	NG	0.7	0.0005

Notes:

NG - Information for contaminant not given

NA - Determine on a site-by-site basis, due to numerous valence states within environment

NA¹ - No C_{leach} value is calculated for this contaminant; refer to appendix B, Table B1 of CALM report

* - USEPA has no consensus Reference Doses or Cancer Slope Factors for inorganic lead, therefore not possible to calculate RBC value.

** - Remanded for Evaluation-Monitoring remains in effect

[a] - Methyl Ethyl Ketone and Lead value obtained from USEPA Region 9 PRG Table

[b] - Ethylbenzene, Antimony and Cadmium value obtained from 40CFR141.61

[c] - Value obtained from Nevada Administrative Code 445A.455

6 References

1. D. D. Gates and R. L. Siegrist. 1995. In Situ Chemical Oxidation of Trichloroethylene using Hydrogen Peroxide. *J. Environ. Engineer.* 121:639-644.
2. U. S. EPA. 1998. In Situ Remediation Technology: In Situ Chemical Oxidation. OSWER, Washington, DC. EPA 542-R-98-008.
3. Final Emergency Removal Plan for SWMU12, Anniston Army Depot, Anniston Alabama; QST Environmental Inc.; October 1998.
4. Full-Scale Soil Remediation of Chlorinated Solvents in Clay Soils by In Situ Chemical Oxidation; R. Levin, and E. Kellar (QST), J. Wilson (GeoCleanse®), L. Ware (ANAD), and J. Findley and J. Baehr (USACE).
5. Report of Findings Concerning UST Occurrence at Building 8049, MCALF, Bogue, Carteret County, NC; Department of Navy, Naval Facilities Command, Atlantic Division; April 13, 1999.
6. Geology and Hydrogeology at CRREL: A Preliminary Site Investigation: Internal Report 1088, May 1991.
7. Draft Final Remedial Investigation Report of Cold Regions Research and Engineering Laboratory, Hanover, New Hampshire; Ecology and Environment; July 1992.
8. Phase II Remedial Investigation for Cold Regions Research and Engineering Laboratory (CRREL) Hanover, NH; Arthur D. Little, Inc.; March, 1994.
9. Innovative Technology Demonstration at the Cold Regions Research and Engineering Laboratory; CRREL, 1998 (?).
10. In Situ Oxidation of Trichloroethylene using Potassium Permanganate, Part 1: Theory and Design; Lachance, J. C., et al, *Oxidation Technologies*.
11. In Situ Oxidation of Trichloroethylene using Potassium Permanganate, Part II: Pilot Study; McKay, Daniel, et al, *Oxidation Technologies*.
12. In-Situ Chemical Oxidation of Trichloroethylene Using Potassium Permanganate; McKay, Daniel; ARCSACC'99.
13. Telephone communication with Mr. Daniel McKay by Mr. Paul Gruntmeyer, July 20, 1999.
14. Telephone communication with Mr. Robert Steddin by Mr. Paul Gruntmeyer, July 20, 1999.

15. Final Report, In Situ Chemical Oxidation/Deep Soil Mixing Demonstration at the Kansas City Plant, S. R. Cline, *et al*, Oak Ridge National Laboratory, September, 1996.
16. Presentation entitled “NSB Kings Bay In-situ Chemical Oxidation and Natural Attenuation for Accelerated/Cost Efficient Cleanup; Clifton C. Casey, P.E., Technical Support and Anthony Robinson, Project Manager.
17. Article entitled “Source Reduction by In-situ Chemical Oxidation at NSB Kings Bay Results in Significant Savings in Time and Cost; Clifton C. Casey, P.E., Technical Support and Anthony Robinson, Project Manager.
18. Final Effectiveness Evaluation Report Geo-Cleanse® Treatment Program; Naval Submarine Base Kings Bay Site 11, Kings Bay, Georgia, Geo-Cleanse® International, Inc.; May 7, 1999.
19. Technical Plan for CERCLA Removal Action: In Situ Remediation of Vadose Zone Soils and a Pilot Study for In Situ Remediation of the Bedrock Aquifer at the PDO OU4 Oil Burn Pit: Letterkenny Army Depot, Chambersburg, Pennsylvania; Roy F. Weston, Inc.; November, 1997.
20. Technical Plan for: an In Situ Chemical Oxidation Remediation Pilot Study of the Bedrock Aquifer at the Southeastern (SE) Disposal Area (DA); Letterkenny Army Depot, Chambersburg, Pennsylvania; Roy F. Weston, Inc., Geo-Cleanse® International, Inc, et al; June 1999.
21. Draft Presentation entitled “ In situ Remediation of Vadose Zone Soils at the Oil Burn Pit, Letterkenny Army Depot, Chambersburg, Pennsylvania; Roy F. Weston, Inc., Geo-Cleanse® International, Inc, 1999.
22. Telephone conversation between Mr. Joseph B. Gormley and Mr. Paul R. Stone III on June 24, 1999 regarding outstanding questions on Letterkenny In Situ projects.
23. Response to Comments from Mr. Joseph B. Gormley from ThermoRetec Corporation Concerning the In Situ Remediation of Vadose Zone Soils at the Letterkenny Oil Burn Pit; Ken Cowan of Roy F. Weston; July 6, 1999.
24. Final In Situ Ozone Sparging Pilot-Scale Testing Report; Site ST-44 Nellis Air Force Base Las Vegas, NV; ERM Program Management Company; October 13, 1997.
25. June 11, 1999 letter from the Naval Facilities Engineering Service Center presenting groundwater monitoring results from the in situ chemical oxidation project at NAS Pensacola, FL.
26. Telephone conversation with Mr. Maxie Keisler, Project Manager, Naval Facilities, Southern Division on July 15, 1999 regarding the Pensacola in situ oxidation project.

27. A Full-scale Demonstration of In Situ Chemical Oxidation Through Recirculation at the X-701B Site: Field Operations and TCE Degradation, Oak Ridge National Laboratory, Environmental Sciences Division Publication No, 4727, December, 1997.
28. Characterization of the Geology, Geochemistry, Hydrology, and Microbiology of the In-situ Air Stripping Demonstration Site at the Savannah River Site (U); C.A. Eddy, B. B. Looney, etal; Westinghouse Savannah River Company; May 1, 1991.
29. Assessing DNAPL Contamination, A/M Area, Savannah River Site: Phase I Results (U); B. B. Looney, etal; Westinghouse Savannah River Company; December 15, 1992.
30. Test Plan for Geo-Cleanse® Demonstration (In Situ Destruction of Dense Non-Aqueous Phase Liquid (DNAPL); Westinghouse Savannah River Company and Geo-Cleanse® International, Inc.; September 1996.
31. Underground Injection Permit Application for Geo-Cleanse® Demonstration Integrated Demo Site at M-Area; Westinghouse Savannah River Company; September 18, 1996.
32. Estimating the Extent and Thickness of DNAPL within the A/M Area of the Savannah River Site (U); D. G. Jackson, T. H. Payne, B. B. Looney, J Rossabi; Westinghouse Savannah River Company; December 20, 1996
33. Final Report for Demonstration of In Situ Oxidation of DNAPL Using the Geo-Cleanse® Technology; K. Jerome, B. Rhia, B.B. Looney; Westinghouse Savannah River Company; September 19, 1997.
34. Presentation on “Inorganic Effects on Aquifer Geochemistry of In Situ Destruction of DNAPL by Fenton’s Reagent”; Savannah River Technology Center and the University of Georgia.
35. Abstract on “Inorganic Effects on Aquifer Geochemistry of In Situ Destruction of DNAPL by Fenton’s Reagent”; Savannah River Technology Center.
36. Abstract on “Effect of Fenton’s Reagent on Subsurface Microbiology and Biodegradation Capacity; J. Kastner, J. SantoDomingo, M. Denham; Westinghouse Savannah River Company.
37. Draft Chemical Oxidation Pilot Test Report, Operable Unit 4; Shaw Air Force Base, Sumter, SC; International Technology Corporation; February 24, 1997.
38. Executive Summary Chemical Oxidation Pilot Test Report, Operable Unit 4; Shaw Air Force Base, Sumter, SC; International Technology Corporation; December 16, 1997.