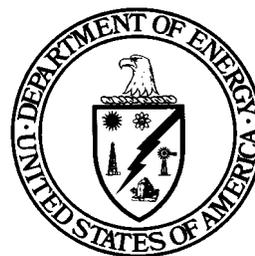


# **INNOVATIVE TECHNOLOGY**

Summary Report DOE/EM-0484

## **Fenton's Reagent**

Subsurface Contaminants Focus Area



*Prepared for*  
U.S. Department of Energy  
Office of Environmental Management  
Office of Science and Technology

October 1999



# Fenton's Reagent

OST/TMS ID 2161

Subsurface Contaminants Focus Area

*Demonstrated at*  
Savannah River Site  
Aiken, South Carolina



## ***Purpose of this document***

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

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

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

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

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# SECTION 1 SUMMARY

## Technology Summary

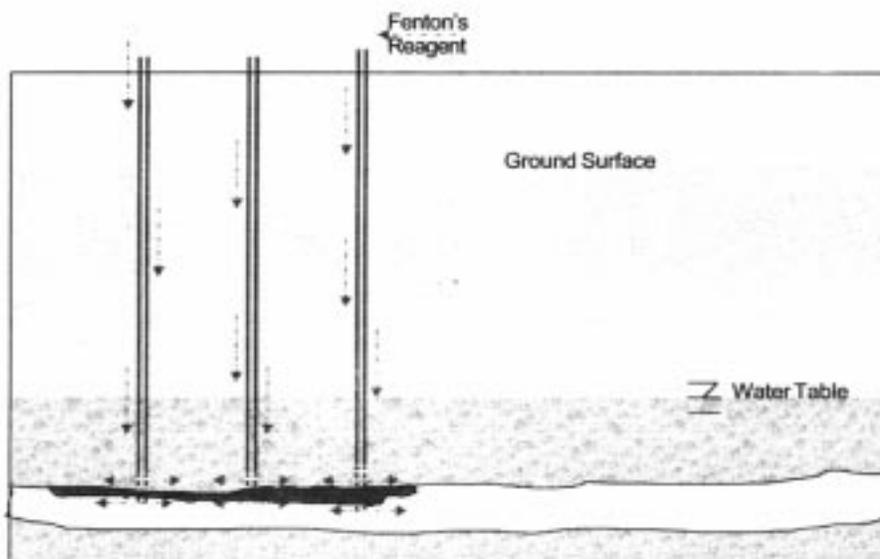
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### Problem

The release of contaminants such as solvents and other volatile organic compounds (VOCs) into surface impoundments or through other disposal practices has resulted in the contamination of the subsurface at numerous DOE and other sites across the nation. These organic contaminants were often introduced to the subsurface as a pure phase that was either lighter than or heavier than water. Those compounds heavier than water, such as solvents, are commonly known as DNAPLs (dense, non-aqueous phase liquids) when they are present as a separate phase. Those compounds lighter than water, such as gasoline, are commonly known as LNAPLs (light, non-aqueous phase liquids) when they are present as a separate phase. DNAPLs are often found both above and below the water table and LNAPLs are found above the water table, near the original source area where the contaminant was introduced into the subsurface. DNAPLs and LNAPLs in the subsurface are difficult to remove by pump-and-treat methods, can be difficult to detect and treat in situ, and act as significant sources of contamination continuously released to the ground water.

### How It Works

- In situ oxidation using Fenton's chemistry (aka Fenton's Reagent) can be utilized to treat DNAPLs in the subsurface. The-Geo-Cleanse<sup>®</sup> process uses hydrogen peroxide ( $H_2O_2$ ) and iron salts where the effectiveness of  $H_2O_2$  is improved by iron through generation of highly reactive hydroxyl radicals. The iron acts as a catalyst in the process; iron typically occurs naturally in the subsurface or may be added in small concentrations.
- During the oxidation of a contaminant many reactions occur. However, the overall reaction consists of a contaminant,  $H_2O_2$ , and ferrous iron, as a catalyst, consumed to produce water, oxygen, and carbon dioxide. By products from the reaction are non-toxic at the levels produced.



**Figure 1. Conceptual schematic of Fenton's Reagent injection for DNAPL treatment below the water table**

- Non-halogenated compounds (e.g., BTEX) are converted to carbon dioxide and water, and
- Halogenated compounds (tetrachloroethylene (PCE) and trichloroethylene (TCE)) are converted to carbon dioxide, water, hydrogen and chloride ions.
- Fenton's Reagent has been widely used in wastewater applications for over 50 years. The technology has since been used to remediate hazardous waste sites with organic-contaminated soils and groundwater. Organics targeted for treatment include:
  - chlorinated solvents (TCE, PCE, TCA, DCA, etc.),
  - munitions,
  - pesticides,
  - petroleum hydrocarbons (BTEX, PAH, TPH, diesel fuel)
  - wood preservatives, and
  - PCBs and phenolics.
- The Geo-Cleanse<sup>®</sup> process, in situ oxidation Using Fenton's Reagent, has been applied to approximately 40 sites, both as initial treatment for source removal and as full-scale remediations. Deployments have occurred at a wide range of sites including:
  - gasoline stations contaminated with BTEX in silty clays and glacial tills (up to 5 inches of free product was removed from one location),
  - chemical manufacturer facilities contaminated with DNAPL compounds in glacial tills and silty clays,
  - an Air Force Base contaminated with chlorinated organics (PCA and DCA) and BTEX in sandy soil, and
  - Department of Defense facilities contaminated with chlorinated organics (TCE, TCA, vinyl chloride, and BTEX) in clays and fractured bedrock.

## Potential Markets

All sites, government and commercial, where solvents and other dense organics were disposed likely contain DNAPLs in the subsurface. Treatment of these DNAPL source zones is critical to the overall remediation strategy at any of these sites. A number of DOE sites, such as SRS and Oak Ridge, have already identified DNAPLs in the subsurface. Others likely have them present but they have not been located during site assessments.

### Advantages Over Baseline

- In situ oxidation using Fenton's Reagent to treat DNAPLs in the subsurface provides a number of advantages over the base-line pump-and-treat technology:
  - minimization of secondary waste and investigation-derived waste (no water is pumped to the surface for treatment),
  - in-place generation of innocuous by-products (water, oxygen, and carbon dioxide),
  - potential to accelerate clean-up activities.
- In situ oxidation using Fenton's Reagent to treat DNAPLs in the subsurface provides a number of advantages over alternative in situ technologies based on solubilization rather than oxidation.
  - Solubilization can promote downward movement of DNAPLs, causing further spread of contamination.

## Demonstration Summary

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- A demonstration of in situ oxidation using Fenton's Reagent was conducted at the Savannah River Site (SRS) in the spring of 1997. This demonstration, sponsored by the Department of Energy, was a cooperative venture between Westinghouse Savannah River Company (WSRC) and Geo-Cleanse International, Inc.

- The site selected for the demonstration was an area of approximately 50 foot (ft) by 50 ft adjacent to a known source of DNAPL; a small DNAPL plume located below the water table was treated over a 6-day period (Figure 1).
- The catalyst solution of 100 parts per million (ppm) ferrous sulfate, pH-adjusted with concentrated sulfuric acid, was initially injected into the subsurface to ensure adequate migration into the formation, while the groundwater pH was adjusted to between 4 and 6. Subsequent injection of the H<sub>2</sub>O<sub>2</sub> and catalyst utilized a patented mixing and injection process. Injections were conducted in batch mode with one batch injected per day. Following 6 days of injection, the site was characterized to determine treatment efficiency.

## Key Results

- During the SRS Fenton's Reagent demonstration, a destruction efficiency of 94% was achieved based on the estimated mass of DNAPL removed as determined by soil sampling.
- Average contaminant concentrations in groundwater in the treatment zone were 119.49 milligrams per liter (mg/l) PCE and 21.31 mg/l TCE before treatment and 0.65 mg/l PCE and 0.07 mg/l TCE at completion of treatment.
- An increase in chloride concentrations was observed in the test area, verifying oxidation of PCE and TCE by the H<sub>2</sub>O<sub>2</sub>.
- As part of the technology evaluation, a unit cost per pound of DNAPL destroyed was determined for sites with different depths to DNAPL and for varying volumes of DNAPL.
- As a result of oxidation of the subsurface, minor metals mobilization was observed. However, concentrations of dissolved metals remained below levels of concern.
- The break-even unit cost for in situ oxidation using the Geo-Cleanse<sup>®</sup> process compared with pump and treat was determined to be dependent on the depth to contamination and total DNAPL mass volume. At SRS, the break-even point ranged from 6500 to 9500 pounds of DNAPL as depth of contamination increased from 60 to 155 feet.
  - Unit cost at sites with small volumes of DNAPL, less than 4000 pounds, is greater than \$100/pound of DNAPL.
  - Unit costs escalate to greater than \$700/pound of DNAPL for sites with approximately 1000 pounds of DNAPL.
- The technology is commercially available from Geo-Cleanse International, Inc.

## Contacts

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**Other**

All published Innovative Technology Summary Reports are available on the OST Web site at <http://em-50.em.doe.gov> under "Publications." The Technology Management System, also available through the OST Web site, provides information about OST programs, technologies, and problems. The OST Reference # for In Situ Oxidation Using Fenton's Reagent is 2161.

## SECTION 2 TECHNOLOGY DESCRIPTION

### Overall Process Definition

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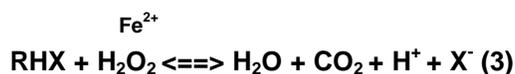
- The Geo-Cleanse<sup>®</sup> process is based on Fenton's Reagent, which uses H<sub>2</sub>O<sub>2</sub> and iron salts. Fenton's Reagent chemistry (1) is well documented as a method for producing hydroxyl radicals by reaction of H<sub>2</sub>O<sub>2</sub> and ferrous iron (Fe<sup>2+</sup>). Hydroxyl radicals are very powerful, effective and nonspecific oxidizing agents, approximately 106 to 109 times more powerful than oxygen or ozone alone.



- With the Geo-Cleanse<sup>®</sup> process, iron salts in the form of ferrous sulfate (Fe<sup>2+</sup>) and H<sub>2</sub>O<sub>2</sub> are injected using a patented process, Patent #5,525,008, to generate hydroxyl radicals.
  - Proprietary mixtures of non-hazardous metallic salts are used to control the reaction.
  - During the optimum reaction sequence with an iron catalyst, ferrous iron (Fe<sup>2+</sup>) is converted to ferric iron (Fe<sup>3+</sup>).
  - Ferrous iron, soluble in water at the target pH, is necessary for generation of the hydroxyl radical. The iron will remain available in ferrous form as long as pH is properly buffered and there is sufficient H<sub>2</sub>O<sub>2</sub>. As H<sub>2</sub>O<sub>2</sub> is consumed, some iron will precipitate out as ferric iron (if pH is moderate).
  - Ferric iron will not generate the hydroxyl radical and is less soluble at the target pH range (pH 5 to 6). Under properly controlled and buffered conditions, ferric iron can be regenerated back to ferrous iron by a subsequent reaction with an additional molecule of H<sub>2</sub>O<sub>2</sub> (2).



- There are many reactions that occur during the oxidation of a contaminant; as shown by equation (3) a contaminant (RHX), H<sub>2</sub>O<sub>2</sub>, and ferrous iron, as a catalyst, are consumed to produce water and carbon dioxide. RHX represents an organic compound and X represents a halide (such as chloride). If the compound is non-halogenated (no X), then the hydrogen ion and halide anion are not formed in the overall reaction. Thus, compounds such as BTEX are converted to carbon dioxide and water, whereas TCE and PCE are converted to carbon dioxide, water, hydrogen and chloride ions, which are all non-toxic at the levels they will be produced.



### System Design and Operation

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Actual system design is dependent upon the specific site geology and hydrology and the distribution of the DNAPL in the sub-surface. For the SRS demonstration: A circular pattern with an injector in the center, ringed by 3 injectors with 3 monitoring wells in a third outer ring was chosen for the demonstration. Injectors were set on 17-foot centers with monitoring wells on 27-foot centers (Figure 2). Five-foot screens with the screen zone set from 138 ft to 143 ft below surface (i.e. the top 5 feet of the treatment zone) were used for all wells. Three vadose-zone piezometers were also installed at the demonstration site.

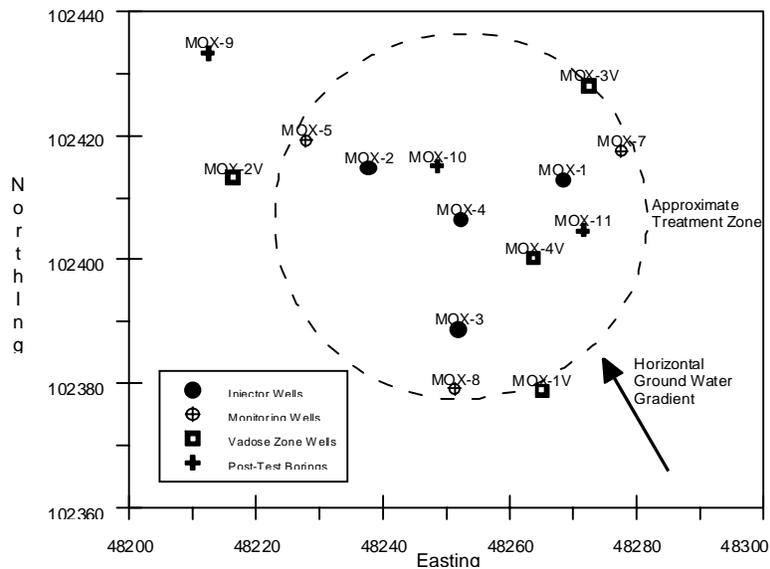


Figure 2. Schematic of Fenton's Reagent field demonstration site layout.

- A key component of this technology is the proprietary injection process (Patent #5,525,008). The injector contains a mixing head for mixing reagents and components to stimulate circulation of groundwater, promoting rapid reagent diffusion and dispersion. All reagents are injected into the subsurface through the injectors. The process maximizes the dispersion and diffusion of the reagent through the soil and or aquifer and the injectors are specially designed to withstand the elevated temperatures and pressures resulting from Fenton's reaction.
- When injection is initiated, air with catalyst solution was injected to ensure the injector was open to the formation prior to injection of  $H_2O_2$  and catalyst solution. When an acceptable flow was established,  $H_2O_2$  and catalyst were injected simultaneously.



Figure 3. Photo of Geo-Cleanse® injection well.

- The injector is designed with a check valve and constant pressure delivery system, which prevents mixing of the chemicals before they have reached the zone of contamination or treatment, eliminating the likelihood of reaction within the wellbore (Figure 3).
- During injection a batch-process operation was performed approximately 6 hours per day, one batch per day.
  - Each day the initial injection consisted of the catalyst solution only.
  - Finally, injection of  $H_2O_2$  and additional catalyst, simultaneously, in volumes varying from 500 to 1000 gallons per batch, completed the injection.
- A tank capable of holding 45,000 pounds of  $H_2O_2$  and a dosing unit for transfer from the tank to the Geo-Cleanse® process equipment were used.

## SECTION 3

# PERFORMANCE

### Demonstration Plan

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- A demonstration of Fenton's Reagent was conducted at SRS in the spring of 1997. This demonstration was a cooperative venture between Westinghouse Savannah River Company and Geo-Cleanse International, Inc.
- This demonstration involved treating a small DNAPL plume below the water table at the SRS in the A/M Area over a 6-day period. A description of the site geology is found in Appendix A.
  - DNAPL, as TCE and PCE, is located at approximately 140 ft below surface at the demonstration site (approximately 15 ft below the top of the water table). The uppermost significant clay beneath the water table, the "Green Clay", is located 30 feet below the water table.
  - The treatment zone was estimated to contain 68,000 cubic feet (ft<sup>3</sup>) of soil containing approximately 600 pounds of DNAPL.
- The treatment zone was considered to be a 27-foot radius circular area (emanating from the central injection well. The vertical extent of the treatment zone extended from the water table to the top of the "Green Clay." The volume of the treatment zone was estimated as 68702 ft<sup>3</sup>.
- Four injector wells, four monitoring wells and four vadose-zone piezometers were installed.
- The demonstration consisted of three stages: pre-test characterization, treatment, and post-test characterization.

### Demonstration Overview

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- Pre-test characterization was used to identify the location of the treatment zone and the initial PCE and TCE concentrations. Pre -test activities consisted of (Figure 2):
  - 8 soil borings sampled and analyzed for PCE and TCE,
  - installation of injection wells in 4 of these soil borings,
  - installation of monitoring wells in the remaining 4 soil borings, and
  - installation of 4 additional vadose-zone piezometers.
- The design of the treatment system, including the number of injectors and volume of H<sub>2</sub>O<sub>2</sub> and catalyst solution, was based on the source volume predicted from site-specific characterization data to ensure sufficient mass of oxidant was delivered to treat the DNAPL through a sufficient number of injection locations.
- Monitoring wells were sampled daily before the injection process began.
- The demonstration was initiated with injection of catalyst solution with 2 to 4 cfm of air to sparge the catalyst away from the injector into the formation. This adjusted the groundwater pH to between 4 and 6, where metals, specifically iron, would be at the optimal valence state, +2. Additionally, this ensured that the injector was open to the formation prior to injection of H<sub>2</sub>O<sub>2</sub> and catalyst solution.
- Injection operations continued for approximately 6 hours per day using 4 injectors for a total of 6 days (Figure 4).
- The H<sub>2</sub>O<sub>2</sub> and catalyst were then injected simultaneously.
  - Mixing of catalyst and H<sub>2</sub>O<sub>2</sub> in the subsurface generated heat as the reaction with organic contaminants progressed.
  - During injection the groundwater was circulated to promote rapid reagent diffusion and dispersion. When an acceptable flow had been established, H<sub>2</sub>O<sub>2</sub> and catalyst were injected

simultaneously. This ensured that the catalyst and H<sub>2</sub>O<sub>2</sub> did not mix together in the sealed system and eliminated the chance of reaction within the wellbore.

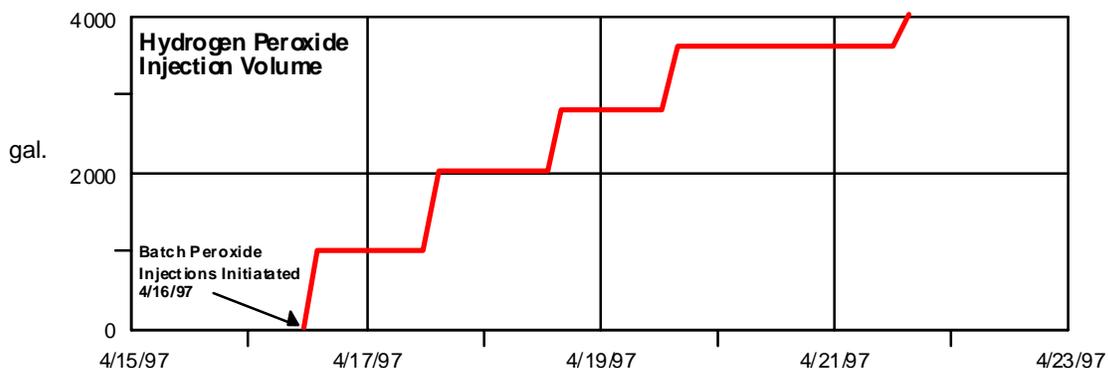


Figure 4. Volume of hydrogen peroxide injected

- Monitoring of off-gases for water vapor, carbon dioxide gas, H<sub>2</sub>O<sub>2</sub>, the contaminants, pH, conductivity, and dissolved oxygen was conducted in monitoring wells throughout the injection process. Water sampling was limited due to poor pump performance caused by gases entrained in the groundwater during and immediately following injections (bubbling was heard emanating from the monitoring wells).
- Three post-test soil borings were collected 3 days after the last injection to determine the effectiveness of the treatment process. Post-test borings were located on a transect running through the test area and within 3 feet of the center of the test zone, with one boring approximately 10 ft outside the outermost monitoring well. The outermost boring was used to verify that the DNAPL had not been moved out of the treatment zone. Weekly sampling and analysis of monitoring wells for several months after the injection process has been completed. Sampling of monitoring wells continued until PCE and TCE concentrations stopped increasing, a period of approximately 3 months.

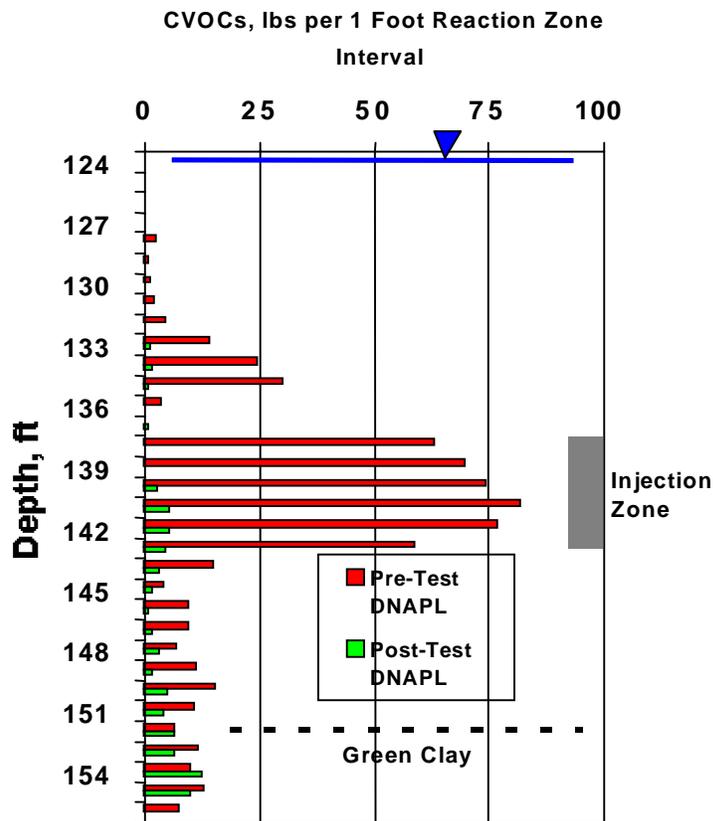
## Results

- During pre-test characterization the majority of the DNAPL was detected in a zone from 138 ft bgs to 144 ft bgs on a clay stringer approximately 10 ft above the "Green Clay" (Appendix A), although small quantities of PCE and TCE were detected below the "Green Clay". Based on these data, the total estimated volume of DNAPL was 593 pounds.
- Average contaminant concentrations in the treatment area groundwater were 119.49 mg/l PCE and 21.31 mg/l TCE before treatment and were reduced to 0.65 mg/l PCE and 0.07 mg/l TCE at completion of treatment.
- Average pH was 5.71 before treatment and 2.44 at completion of treatment. Change in pH was due to addition of acid to maintain optimal oxidation conditions and, to some extent, due to production of CO<sub>2</sub> from the oxidation process. After 17 months, pH has risen to 3.4 to 4.0.
- Average baseline groundwater temperature in the treatment zone was 19.2°C; this was raised to a maximum of 34.7°C by the oxidation process.
- Dissolved oxygen concentrations increased from an average of 9.3 mg/l before treatment to 24 mg/l after treatment.
- Average baseline chloride concentration was 3.61 mg/l; chloride reached a maximum of 24.33 mg/l at the completion of the treatment process. The increase in chloride concentration verified oxidation of PCE and TCE by the peroxide.
- Hydrogen peroxide concentrations in the monitoring wells ranged from approximately 2 to 5 ppm.

- Monitoring of gases in the headspace of monitoring wells for CO<sub>2</sub>, PCE, and TCE during the injection process indicated:
  - Gases were escaping from water in the monitoring wells during injection due to the violent oxidation process.
  - Carbon dioxide levels in these gases rose to over 3,500 ppmv (ambient CO<sub>2</sub> levels are approximately 300-400 ppmv). Elevated CO<sub>2</sub> levels verified DNAPL oxidation in the subsurface.
  - PCE (from 0 to 190 ppmv) and TCE (0 to 80 ppmv) were evident in the vapor and can be attributed to sparging of water in the wells.
- The estimated pre-test mass of DNAPL in the treatment zone was 593 lbs; the estimated post-test mass of DNAPL was 36 lbs (Table 1, Figure 5). Estimated destruction of contaminants in the treatment zone, defined as the vertical distance between the water table (124 ft bgs) and the "Green Clay" (152 ft bgs) and a 27 ft radius around the center injector, was 94%.

**Table 1. Calculated pre- and post-test DNAPL mass and destruction**

Location	Pre-Test, lbs			Post-Test, lbs			Destruction		
	PCE	TCE	Total	PCE	TCE	Total	PCE	TCE	Total
Above the "Green Clay"	528.53	64.56	593.1	28.24	7.95	36.19	94.7%	87.7%	93.9%
Below the "Green Clay"	36.23	13.07	49.30	26.96	9.98	36.94	25.6%	23.6%	24.5%



**Figure 5. Pre- and post-test DNAPL mass for the SRS Fenton's Reagent demonstration**

- Groundwater concentrations of PCE and TCE began rebounding in the monitoring wells within one year after treatment was completed. Rebound in the treatment zone can be attributed to groundwater coming into equilibrium with small DNAPL globules not treated. Some of the small DNAPL globules in the fine-grained sediments were probably not contacted by the hydrogen peroxide and were therefore not oxidized during the short test period. Rebound can also be attributed to influx from the untreated portions of the plume.
- The indigenous microbial population in the groundwater was significantly affected by the treatment and remained so for a period of one year, when direct counts were two orders of magnitude lower than in the untreated area. Microcosm experiments using treated-zone groundwater demonstrated limited bacterial growth and no significant degradation of the remaining TCE, even after addition of co-metabolic inducers. It is believed that methanotrophic growth and associated TCE degradation is limited by the low pH of the treated groundwater.
- Minor mobilization of metals (Mn=7mg/l, Cu=5mg/l) was observed downgradient of the treatment zone. Core-samples chemistry and textural analyses suggest that metal mobilization was not extensive.

## SECTION 4

# TECHNOLOGY APPLICABILITY AND ALTERNATIVES

### Competing Technologies

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- Pump and treat (using air stripping) is considered the baseline technology for DNAPL-contaminated groundwater.
- Other innovative technologies with potential application for treatment of groundwater contaminated with DNAPLs include:
  - enhancements to pump and treat technologies such as pulsed pumping, high vacuum extraction, or steam flooding,
  - in situ air sparging,
  - reactive barrier walls,
  - in situ soil flushing,
  - in situ oxidation (e.g., ozone and potassium permanganate),
  - in situ bioremediation

### Technology Applicability

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- Fenton's Reagent can be used to treat a wide range of organic contaminants in soil and groundwater including chlorinated solvents, petroleum hydrocarbons, semi-volatile organics, and pesticides.
- Fenton's Reagent is applicable for:
  - (1) In situ destruction of DNAPL, LNAPL, or dissolved organic contaminants in groundwater, at sites with:
    - hydraulic conductivity greater than  $10^{-8}$  centimeters per second (cm/s),
    - depth to groundwater greater than 5 ft, and
    - less than 6 inches of free product (apparent thickness) on the water table.
  - (2) In situ destruction of organic contaminants in soil coupled with enhanced enabling methods (e.g., vertical/horizontal sparging, recirculation wells, deep soil mixing).
- In situ application reduces exposure of workers, minimizes impacts due to site constraints, and typically costs less. Ex situ application provides greater process control and reduced risk of leaching contaminants or degradation products in the groundwater.
- Depth is a major contributor to overall remediation costs when this technology is employed. Other factors contributing to the decision to use this technology include:
  - volume of contaminant plume to be treated
  - end cleanup goals.
- Fenton's Reagent is typically not applicable for:
  - sites where greater than 6 inches of free product is present,
  - areas with high organic carbon content below the topsoil or where contaminants are sorbed to organic-rich materials, and
  - sites where the pH is greater than 8 (Alkaline environments may not be suitable or may require pre-treatment to bring the pH into optimum range).
- Groundwater hardness or carbonate content greater than 400 may not be suitable to treatment.
- Benefits of in situ oxidation using Fenton's Reagent include:

- the reagent ( $H_2O_2$ ) is readily available, inexpensive, and results in the reaction products water, oxygen, and carbon dioxide,
- the chemistry of the process is well known and has been widely used in wastewater treatment applications,
- the process is easily applied and controlled,
- the treatment times and reaction times are rapid, and
- there is no secondary waste stream produced and the degree of treatment can be regulated and easily combined with other processes.

### **Patents/Commercialization/Sponsor**

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- In Situ Oxidation using Fenton's Reagent is commercially available. The SRS demonstration was conducted using the Geo-Cleanse<sup>®</sup> injection process, patented under U. S. Patent #5,525,008 by Geo-Cleanse<sup>®</sup> International, Inc.

## SECTION 5 COST

### Methodology

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- The cost information presented here is based on the Fenton's Reagent demonstration conducted at SRS in 1997. The total demonstration cost was approximated \$500K.
- A cost comparison of Fenton's Reagent versus pump and treat (air stripping), which is considered a baseline technology for DNAPL-contaminated groundwater, was completed.
  - For the A/M Area at SRS, a DNAPL source area of approximately 11,000 pounds or more was required for this technology to be more cost efficient than pump and treat.
  - Tasks associated with site preparation are expected to remain essentially constant. Implementation of this technology does not require permanent infrastructure such as a permanent power source, permanent water and chemical tanks, etc. However, temporary power and a constant supply of water for the process, as well as for emergency purposes, is required.
  - Pre-test drilling and characterization costs will vary according to site characteristics.
  - Sampling and analyses costs vary linearly with depth to contamination.
  - Costs for the technology treatment (\$148,500) were the largest component of the treatment operation.
  - Post-test drilling and characterization costs, as with pre-test characterization costs will be dependent on depth.
  - Post-test demobilization costs were a small fraction of the entire project costs and included: removal of water tanks, disconnecting the power supply, removal of the generator, and disassembly of secondary containments.

### Cost Analysis

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- At SRS the unit cost for pump and treat using air stripping is currently \$87/pound of DNAPL (this is related to groundwater concentration; the unit cost will increase over time as the concentrations decrease). Thus, the break-even unit cost for In Situ Oxidation using the Geo-Cleanse® process compared with pump and treat was determined. The break-even point is dependent on depth to contamination and at volumes ranging from 6,500 pounds to 9,500 pounds of DNAPL as depth to contamination increases from 60 to 155 ft (Appendix A).
  - Unit cost of In Situ Oxidation at sites with small volumes of DNAPL, less than 4000 pounds, is greater than \$100/pound of DNAPL.
  - Unit costs escalate to greater than \$700/pound of DNAPL for sites with approximately 1000 pounds of DNAPL.
- Unit costs for remediation technologies are often compared on a \$/ft<sup>3</sup> of soil treated. The \$/ft<sup>3</sup> of soil treated was calculated at the \$/lb DNAPL break-even point between Fenton's Reagent and pump and treat for the three depths evaluated. The unit costs on a \$/ft<sup>3</sup> basis are \$8.84/ft<sup>3</sup>, \$9.95/ft<sup>3</sup> and \$13.03/ft<sup>3</sup> for depths of 60 ft, 100 ft and 155 ft to DNAPL contamination, respectively (Table 2).

**Table 2. Unit Cost/Pound of DNAPL Destroyed for Implementation of Fenton's Reagent for Destruction of DNAPL as a Function of Depth to Contamination**

DNAPL (lbs)	UNIT COSTS (\$/lb DNAPL)		
	60 ft depth	100 ft depth	155 ft depth
500	708	816	917
1,000	365	419	469
2,000	194	221	246
5,000	105	116	126
6,000	92	101	109
6,750	84	92	99
7,500	78	85	92
9,000	79	85	90
10,000	73	78	83
11,000	68	73	78
12,000	65	69	73

**Table 3. Costs for Fenton's Reagent SRS Demonstration**

<b>Activity Category/Task</b>	<b>Cost</b>
<b>Site Preparation and Operation Activities</b>	
Construct Secondary Containments	\$10,425
Generator Rental	\$6,456
Electrical Hookup	\$12,411
Signs	\$5,098
Tanks Setup	\$11,081
Water Supply	\$4,320
Clearing/Grubbing	\$10,631
	<b>\$60,422</b>
<b>Pre-test Drilling and Characterization</b>	
Drilling Subcontract	\$85,000
Oversight and Sampling (provided by WSRC)	\$44,070
Analysis	\$19,229
Sampling Supplies	\$2,439
	<b>\$150,738</b>
<b>Treatment</b>	
Oversight	\$14,627
Peroxide	\$20,412
Operation	\$148,500
	<b>\$183,539</b>
<b>Post-test Drilling and Characterization</b>	
Drilling Subcontract	\$22,000
Oversight and Sampling	\$20,888
Analysis	\$6,589
	<b>\$49,477</b>
<b>Post-test Demobilization</b>	
Disconnect Electrical Hookups	\$2,677
Tear down secondary containments	\$2,764
Remove generators	\$1,493
	<b>\$6,934</b>
<b>Documentation and Project Management</b>	
Documents	\$36,003
Project Management (provided by WSRC)	\$24,002
	<b>\$60,005</b>
<b>TOTAL</b>	<b>\$511,115</b>

## **Cost Conclusions**

- Cost for the treatment technology was the largest component of the demonstration cost.
  - The majority of these costs are labor and equipment use and are based on duration of the work.
  - Peroxide costs were \$20,412 for 42,000 pounds of peroxide.
  - The controlling factor was the amount of contaminant present at the site (estimated at ~600 pounds for this demonstration).
  - Project oversight costs were also associated with treatment operations and were dependent on duration of treatment

- Depth to contamination and amount of DNAPL present will be driving factors in determining costs for use of this technology for in situ groundwater treatment.
  - Pre-test drilling and characterization costs will vary according to site characteristics. Drilling costs include drilling, well installation, well materials, and well completion. At SRS, they were approximately \$70/ft.
  - Peroxide costs \$0.50/pound and its usage was based on 42 pounds of H<sub>2</sub>O<sub>2</sub> per pound of DNAPL. Thus, the cost of H<sub>2</sub>O<sub>2</sub> per pound of DNAPL present is \$21.
    - For a small site (i.e. 2,000 pounds of DNAPL), peroxide costs will not be a significant portion of the entire remediation costs, less than 10%
    - For a large site (i.e. 15,000 pounds of DNAPL), the peroxide costs can be a significant portion of the total remediation costs, 20% and greater..
- Documentation and project management costs were approximately 12 percent of the demonstration, with 5 percent of total costs going to project management activities and 7 percent of total costs attributed to documentation activities. Documentation included a test plan, all regulatory documents for drilling and underground injection, scopes of work for drilling services and other materials, and a test report documenting the results of the demonstration.

## SECTION 6

# REGULATORY AND POLICY ISSUES

### Regulatory Considerations

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- Permit requirements for the demonstration were controlled by the South Carolina Department of Health and Environmental Control.
- Specific permits for this technology depend on the specific application and state/federal requirements. Early and continuous discussions with the regulators will encourage more rapid permitting.
  - An Underground Injection Permit will likely be required.
  - Well installation and completion permitting or an “injector permit” (similar to monitoring well permits) may be required by local and state agencies for installation of the injector access casing (for this demonstration only a monitoring well permit was required).
  - Comprehensive Environmental Recovery, Compensation, and Liability Act (CERCLA) or Resource Conservation and Recovery Act (RCRA) permitting may be required. The SRS project did not address the 9 CERCLA criteria, as it was only a demonstration. However, many of the nine criteria are addressed in other sections of this report.
  - At federal facilities a National Environmental Protection Act (NEPA) review is required.

### Safety, Risks, Benefits, and Community Reaction

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#### Worker Safety

- The reaction can be vigorous with rapid evolution of oxygen, steam and carbon dioxide. Allowances should be made to ensure adequate venting of these gases.
- All field personnel must be 40-h Occupational Safety and Health Administration (OSHA) trained as required in 29 CFR 1910.120 for hazardous waste operations.

#### Community Safety

- The materials injected ( $H_2O_2$  and ferrous iron) pose no hazard to the community due to their low concentration after dispersal into the soil or groundwater.
- The community is not exposed to harmful by-products as the overall reaction results in generation of water, oxygen, carbon dioxide, and halides (when chlorinated solvents are present).
- Fenton's Reagent does not produce release of volatile organic compounds.
- No unusual or significant safety concerns are associated with transport of equipment or other materials associated with this technology.

#### Environmental Impacts

- Hydrogen peroxide and ferrous iron are safe in the environment due to their low concentration after dispersal into the soil or groundwater.
- There is no environmental impact due to the by-products of the reaction: water, oxygen, carbon dioxide, and halides (when chlorinated solvents are present).
- Eventually iron will precipitate out as the insoluble form of iron. This process will not adversely impact groundwater. The Geo-Cleanse<sup>®</sup> process has been widely used for LNAPLs; adverse impacts due to precipitation of iron have not been observed.

### **Socioeconomic Impacts And Community Perception**

- Fenton's Reagent has minimal economic or labor force impacts.
- The general public has limited familiarity with Fenton's Reagent; however, the technology can be explained to the public with ease similar to that of wastewater treatment technologies.

## SECTION 7

# LESSONS LEARNED

### Design Issues

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- Typical treatment ratios for reagent ( $\text{H}_2\text{O}_2$ ):contaminant range from 5 to 50:1 for soil treatment and 1 to 5:1 for aqueous treatment. The efficiency of the process increases at higher contaminant concentrations and decreases as target treatment levels become more stringent.
- Higher  $\text{H}_2\text{O}_2$  concentrations provide faster reaction times, significantly greater removal of DNAPL-type contaminants, but less efficient  $\text{H}_2\text{O}_2$  use.
- Highly alkaline soils may require mineral acid addition to bring the pH into the optimal range.
- Organic carbon content may impact treatment because the hydroxyl radical is relatively non-selective. However, no significant effect was observed with contaminant levels of 500-2000 ppm with total organic carbon of 0.1 to 1.3 (Watts, et al. 1994. "On site treatment of contaminated soils using hydrogen peroxide." Project Report T9234-06, Washington State Transport Center, Washington State University).
- For in situ groundwater treatment, the number and pattern of injectors and monitoring wells must be designed to ensure maximum coverage of the treatment zone. Because the cost is related to depth (cost per well was approximately \$70/ft) and amount of DNAPL, the number and spacing of the wells becomes critical. The heterogeneity of the subsurface at the site will also control the number and spacing of wells required.
- Duration of operation is not a linear function of volume of DNAPL. Factors affecting the duration of the treatment include: permeability, heterogeneity, and geochemistry of the aquifer.

### Implementation Considerations

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- When implementing in situ oxidation using Fenton's Reagent, general operation considerations include:
  - pH of the system must be between 3 and 6.
  - The rate of the reaction increases with increasing temperature (although the efficiency declines above 40 to 50°C)
  - For most applications the valence of the iron salts used doesn't matter (+2 versus +3) nor does it matter whether a chloride or sulfate salt of the iron is used, although chlorine salts may generate high rates of chloride during application.
  - Due to oxidation of the subsurface, metals that are mobile under these conditions may be released at some sites. This should be considered during the technology selection process.
- Implementation of this technology does not require permanent infrastructure, such as a permanent power source (temporary power is required), permanent water and chemical tanks, etc. Temporary power is required for operation of the system. This is much less expensive for the short duration of operation, typically less than 1 month and in many instances 1 to 2 weeks. Also required is a constant supply of water for process, as well as emergency, purposes. For remote sites where a distribution line with potable water is not available tanks for water storage are appropriate. During the demonstration, approximately 1000 gallons of water per day were used for a 6-day period.
- The end products of in situ oxidation are very appealing. No waste is generated from the treatment process, and no material is brought to the surface.
- At complex sites in situ oxidation Using Fenton's Reagent should be considered in tandem with other technologies. For example, if in situ bioremediation is considered as a polishing step, the pH should be held above 4.0 during the treatment operations.

## Needs for Future Development

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- The effects on the aquifer geochemistry and microbiology in the treatment zone need to be better understood. Because in situ oxidation is a very robust chemical reaction, a reasonable assumption is that most of the microbial population was destroyed during the reaction. The type of microbial activity that will return to the area and to what extent is not known.
- During the demonstration, the pH dropped dramatically from an average pH of 5.7 before treatment to 2.4 at completion of treatment. Post-test treatment has shown a very slow rebound of the groundwater pH. Three months after completion of the test, the groundwater pH remained at approximately 3.5.

## Technology Selection Considerations

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- Depth is a major factor when selecting this technology for deployment. Other factors contributing to the decision include:
  - organic carbon content,
  - the pH range (alkaline environments may not be suitable or require pre-treatment to bring the pH into optimum range),
  - groundwater hardness or carbonate content,
  - volume of DNAPL,
  - probability of greater than 6 inches of free product present,
  - cleanup goals, and
  - heterogeneity of the subsurface

## APPENDIX A

### DEMONSTRATION SITE CHARACTERISTICS

- The Savannah River Site's (SRS) historical mission has been to support national defense efforts through the production of nuclear materials. Production and associated research activities have resulted in the generation of hazardous waste by-products now managed as 266 waste management units located throughout the 300 mile<sup>2</sup> facility.
- The M-Area of SRS was a fuel and target fabrication facility. The mission of this area was processing uranium, lithium, aluminum and other materials into fuel elements and targets for use in the nuclear production reactors. The processes were primarily metallurgical and mechanical, such as casting, extrusion, plating, hot-die-sizing, welding and magneforming. Solvent cleaning and acid/caustic etching were used to prepare the materials.
- The M-Area Settling Basin and associated areas (the overflow ditch, Lost Lake, the seepage area, and the inlet process sewer line), designated as the M-Area Hazardous Waste Management Facility, received process effluent from 1958 until 1985. VOC contamination of soils and groundwater occurred in M-Area as a result of breaks in the old process-sewer line and disposal to the basin. In 1985, a pump and treat system was installed, followed by a soil vapor extraction system in 1995. The M-Area Settling Basin, capped in 1988 and closed under RCRA, is a certified closure as a landfill. These activities have been performed under a RCRA Post Closure Care Part B Permit. This demonstration of an In Situ Oxidation technology to destroy DNAPL supports the phased remediation of the 1500-acre VOC plume.
- A wide range of research and development activities have been performed in support of the A/M-Area groundwater corrective action. These various activities have been designated the Integrated Demonstration and include use of horizontal wells for remediation, an in situ air stripping test, in situ bioremediation test, off gas treatment technology tests, a radio frequency heating test, and an ohmic heating test. Development and demonstration of characterization tools have also been an integral part of the program in the A/M area.

### **Contaminant Locations and Hydrogeologic Profiles**

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#### **Savannah River Site Demonstration**

- The geology in the A/M-Area is characterized by 200 ft of alternating units of permeable sands with low fines and significantly less permeable clayey sand and clay units. The water table is located at approximately 130 ft below ground surface (bgs).
- The sand units range from fine-to coarse-grained and are generally moderately sorted with relatively little silt and clay. Interbedded with the sands are silty clay or clayey sand units, which exhibit relatively low permeabilities. Generally, the clays tend to be thin and discontinuous. In A/M-Area, there are several clay-rich intervals above the water table (about 40 ft bgs, 60 feet bgs, and 95 feet bgs).
- The uppermost significant clay beneath the water table is termed the "Green Clay". This confining zone is at a depth of approximately 30 feet below the water table.
- During routine sampling using a bottom-filling bailer, a separate, dense phase was identified in monitoring wells MSB-3D and MSB-22 sumps. These wells are located approximately 20 feet from the M-Area Settling Basin. The relatively thick vadose zone, approximately 130 ft, beneath A/M-Area tends to limit the downward flux of DNAPL and capture some DNAPL in layered clays. Data collected at separate times suggest that DNAPL below the water table occurs as relatively diffuse ganglia and/or a thin layer on the top of aquitards, and that DNAPL collects in well sumps as a result of dynamic processes. One such process is accumulation of dense ganglia in the well sump as the well is actively purged and sampled (similar to accumulation of sediments in the sump).

- In support of this demonstration, the cone penetrometer, in conjunction with conventional coring, allowed refinement of the delineation of an important clay zone (the "Green Clay") beneath the water table. Undulations and other structural variations on top of this layer serve to control movement of a dense phase below the water table.
- Characterization data indicate a substantial amount of DNAPL has been trapped in clays and silts in the vadose zone above the water table and suggest DNAPL below the water table in A/M-Area is present as disconnected ganglia, rather than as a large, solvent-saturated layer. DNAPL present below the water table is composed of approximately 95% TCE, 5% PCE and a very small but measurable amount of PCBs.

## APPENDIX B REFERENCES

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