Modified Fenton's Processes for Effective In-Situ Chemical Oxidation— Laboratory and Field Evaluation

Prasad K. Kakarla

Thomas Andrews

Richard S. Greenberg

David S. Zervas

ABSTRACT

Fenton's reagent in its conventional form, although effective for contaminant treatment, is impractical from an in-situ field application perspective due to low pH requirements (i.e., pH 3-4), and limited reagent mobility when introduced into the subsurface. Modified Fenton's processes that use chelated-iron catalysts and stabilized hydrogen peroxide have been developed with the goal of promoting effective in-situ field application under native pH conditions (i.e., pH 5-7), while extending the longevity of hydrogen peroxide. Laboratory experiments conducted in soil columns packed with organic soil to compare modified Fenton's catalysts with conventional catalysts (acidified iron [II]) indicated superior mobility and sorption characteristics for modified Fenton's catalysts. Furthermore, the acidic pH of a conventional catalyst was buffered to the native soil range, leading to increased iron precipitation/adsorption following permeation through the soil column. The chelates present within the modified Fenton's catalyst showed greater affinity toward iron compared with the native soil and, hence, minimized iron loss through adsorption during the permeation process even at pH 5-7.

Field effectiveness of the modified Fenton's process was demonstrated at a former dry-cleaning facility located in northeast Florida. Preliminary laboratory-scale experiments were conducted on soil-slurry and groundwater samples to test the process efficacy for remediation of chlorinated solvents. Based on successful experimental results that indicated a 94 percent (soil slurry) to 99 percent (groundwater) reduction of cis-1,2-DCE, PCE, and TCE, a field-scale treatment program was initiated utilizing a plurality of dual-zone direct push injection points installed in a grid fashion throughout the site. Results of treatment indicated a 72 percent reduction in total chlorinated contamination detected in the site groundwater following the first injection event; the reduction increased to 90 percent following the second injection event. © 2002 Wiley Periodicals Inc.

INTRODUCTION

Although Fenton's chemistry is more than 100 years old, field application for in-situ contaminant remediation was not seriously conducted until the last five to seven years. Numerous previously published articles demonstrate the strong reactivity of Fenton's reagent with hazardous compounds present in soil and groundwater, resulting in effective contaminant destruction (Watts et al., 1990; Tyre et al., 1991; Gates et al., 1995; etc.). A traditional Fenton's reaction involves the catalytic decomposition of hydrogen peroxide to form intermediate free radicals, which have an oxidation potential greater than peroxide itself. The fundamental Fenton's reaction mechanism has been well documented in articles by Walling et al. (1975) and Watts et al. (1990). The classic Fenton's reaction is described below:

$$H_2O_2 + Fe^{2+} \rightarrow OH\cdot + OH^- + Fe^{3+} \qquad (1)$$
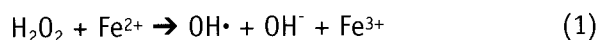
where OH· is the principal oxidizing species known as hydroxyl radicals, which have a potential for contaminant destruction that is one of the highest known in oxidation chemistry literature (Dorfman & Adams, 1973). Many common contaminants including petroleum and chlorinated compounds can be oxidized in a matter of hours using an appropriate treatment stoichiometry consisting of catalyst and hydrogen peroxide. An effective treatment stoichiometry for in-situ Fenton's oxidation is influenced by variables such as pH, contaminant concentration, and total organic carbon (TOC) of the soil being treated. A pH in the range of 3 to 4 has been described as ideal for free-radical generation (Watts et al., 1990). While this holds true when a traditional Fenton's catalyst such as acidified iron (II) or iron (III) salt is used, replicating the acidic pH under field conditions is impractical due to the enormous buffering capacity associated with most native soils. Subsequent work by In-Situ Oxidative Technologies Inc. (ISOTEC^SM) (Greenberg et al., 1998) and others (Rodgers et al., 2001) has demonstrated that free-radical generation and contaminant oxidation can be promoted without acid addition using modified Fenton's catalysts that are effectively chelated in the pH range of 5 to 7, which is more practicable from an in-situ application standpoint. Other factors affecting Fenton's processes in the subsurface are (1) contaminant concentration, which influences the molar ratio and concentration of catalyst and peroxide required for complete oxidation, and (2) soil TOC content, which affects the process by promoting peroxide-consuming reactions. Since oxidizing conditions in the subsurface are never pristine, numerous competing reactions may occur during in-situ application of Fenton's reagent.

Physicochemical Processes in the Subsurface

Catalysts and oxidizers injected into the subsurface are subject to a variety of physicochemical processes including pH buffering, adsorption, precipitation and decomposition reactions. As described by Kakarla and Watts (1997), surface application of hydrogen peroxide can have significant influence only in the top few centimeters of a soil due to competing reactions in the soil that quickly consume residual hydrogen peroxide. Based on prevailing subsurface conditions, hydrogen peroxide may be decomposed to either free radicals or molecular oxygen (Schumb et al., 1955). This is catalyzed by natural organic enzymes (e.g., catalase, peroxidase, etc.) and transition metal elements present in the soil (e.g., Fe, Mn, etc.). The ability of hydrogen peroxide to decompose to oxygen has been used to promote in-situ aerobic bioremediation processes (Pardieck et al., 1992). The corresponding reaction pathway is described below.

$$H_2O_2 \rightarrow \tfrac{1}{2} O_2 + H_2O \qquad (2)$$

However, oxygen generation is not the desired pathway for in-situ chemical oxidation processes due to oxygen's inability to directly oxidize the contaminants—a characteristic that may be attributed to the absence of stable catalysts that are capable of disrupting the oxygen-oxygen multiple bonds. By creating subsurface reaction conditions that ensure the dominance of intermediate free-radical generation over direct oxygen generation, in-situ chemical oxidation using modified Fenton's is becoming highly desirable for environmental remedial applications.

The form and availability of the catalysts is also critical to promote a Fenton's reaction. Iron salts are the most commonly used catalysts in a Fenton's reaction; however, the presence of large concentrations of iron in the native soil does not warrant contaminant oxidation when hydrogen peroxide is injected into the soil. The free-radical generation from hydrogen peroxide occurs by Fenton's process primarily under reaction conditions that ensure the availability of iron in ionic form in a dissolved state. A traditional Fenton catalyst (i.e., acidified iron [II] or iron [III]) introduced into the subsurface is immobilized within inches from the point of injection due to the pH buffering capacity of native soils from the desired acidic conditions to more natural, near-neutral pH conditions (i.e., pH 5-7). These natural, high-pH conditions in turn lead to precipitation of soluble irons, which are the key components promoting the Fenton's reaction. Therefore, the lack of a mobile catalyst translates into an ineffective remedial process for in-situ applications. Hence, a need was realized for effective modified Fenton's catalysts that maintain iron in soluble form under natural conditions while simultaneously promoting free-radical generation.

Modified Fenton's Processes

ISOTEC[SM] developed proprietary modified Fenton's catalysts (protected by U.S. patents) that are effectively chelated to prevent iron precipitation under natural subsurface conditions. The modified Fenton's process facilitated successful field application of Fenton's reagent by mitigating the mobility, pH, and longevity concerns associated with traditional reagents. The modified Fenton's catalyst is prepared at natural pH conditions (i.e., pH 5-7), which prevent significant pH fluctuations when introduced into the subsurface due to native soil buffering. In addition, the ligand molecules within the chelated catalyst have greater affinity toward the iron compared with other metals, thereby preventing iron loss through adsorption to the soil. Research completed with the resultant catalytic reagent was found to have significantly higher mobility compared with conventional Fenton's catalysts. In addition, hydrogen peroxide mixed with stabilizing compounds and introduced at diluted concentrations (between 5 percent to 20 percent) was found to have better treatment efficiency during in-situ remediation compared with high concentrations of peroxide, presumably due to free-radical scavenging by excess peroxide. Not only did stabilized low concentrations of peroxide have better half lives relative to higher concentrations, they also provided a safer working environment during in-situ application.

Recent research (Watts et al., 1999; Kim & Kong, 2002) has demonstrated that modified Fenton's processes promote coexisting oxidation-reduction reactions by producing reductants such as superoxide radical anion ($O_2 \cdot^-$) or hydroperoxide anion (HO_2^-) in addition to oxidation by hydroxyl ($OH \cdot$) radicals alone. In modified Fenton's systems, the following reactions occur beyond the hydroxyl-radical-generating reaction (1) described earlier (Watts et al., 1999):

$$H_2O_2 + OH \cdot \rightarrow HO_2 \cdot + H_2O \qquad (3)$$

$$HO_2 \cdot \rightarrow H^+ + O_2 \cdot^- \qquad (4)$$

$$HO_2 \cdot + O_2 \cdot^- \rightarrow HO_2^- + O_2 \qquad (5)$$

> The modified Fenton's process facilitated successful field application of Fenton's reagent by mitigating the mobility, pH, and longevity concerns associated with traditional reagents.
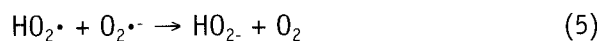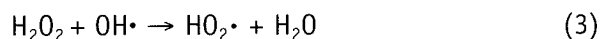
The superoxide and hydroperoxide anions were reported to be responsible for promoting desorption and degradation of recalcitrant organic contaminants. These findings are especially critical toward treatment of contaminants, such as carbon tetrachloride, hexachloroethane, and chloroform, that are known to have relatively low reactivity towards hydroxyl radicals and hence were not considered treatable by traditional Fenton's reagent.

The purpose of this article is to demonstrate the laboratory and field application of the ISOTEC[SM]-modified Fenton's process toward remediation of soil and groundwater. Laboratory experiments, which compare the sorption, mobility, and pH characteristics of modified Fenton's catalysts with conventional acidified iron (II) catalyst, are presented. A recent case study using temporary direct-push injection mechanisms, which demonstrated the laboratory and field applicability of modified Fenton's process, is presented.

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MATERIALS AND ANALYSES

All chemicals used for experimental purposes were American Chemical Society (ACS) reagent grade. Hydrogen peroxide (35 percent) was purchased from Aldrich (WI). All component chemicals required for proprietary ISOTEC[SM]-modified Fenton's catalyst (chelated iron complex) preparation were purchased from Aldrich (Milwaukee, WI) and Fisher Scientific (Fair Lawn, NJ). Bulk quantities of chemicals used during field application were industrial grade and purchased from local distributors. Hydrogen peroxide and iron field-monitoring test kits were purchased from Hach (Loveland, CO). Distilled water was purchased from Wissahickon (Manheim, PA).

Laboratory iron concentrations for soil column studies were determined using the orthophenanthroline spectrophotometric technique (Standard Methods, 1989). Total dissolved solids (TDS) and pH measurements during the field treatment program were conducted using a Myron L. Company (Carlsbad, CA) Ultrameter. In addition, qualitative tests for hydrogen peroxide and iron, utilizing the Hach test kits or equivalent, were conducted during the field treatment program. The field treatment program effectiveness was monitored by measurement of volatile organic compounds (VOCs), which were analyzed using EPA Method 8021. The laboratory treatability study samples were analyzed for VOCs using EPA Method 8260/624.

EXPERIMENTAL SECTION

Mobility/ Sorption Experiments

Soil columns utilized for research on catalyst mobility and sorption characteristics were identical to those described by Kakarla and Watts (1997). The columns (3.2 cm I.D.) were prepared from Schedule 40 polyvinyl chloride (PVC), used in lengths of 30 cm each for experimental purposes. The tops of the PVC columns were left open, while the undersides were fit with perforated PVC caps to allow for eluent drainage. The columns were internally lined with chemically inert Tedlar (PTFE) sheeting (DuPont, NY). A typical soil column was packed using a high-organic soil obtained from northern New Jersey in increments of 50 grams, with exactly 10 taps given to the

column between each increment. This ensured uniformity in the columns packed during comparison experiments.

Experiments to compare the sorption and mobility characteristics of modified Fenton's catalyst with acidified iron (II) catalyst were conducted using three pairs of columns packed at three different depths. Column pair #1 was packed using 100 g of soil, column pair #2 using 200 g of soil, and column pair #3 using 300 g of soil. The corresponding post-packing depths of each column pair were determined to be approximately 6.2 cm, 13 cm, and 20 cm, respectively. The catalyst solutions were prepared to obtain an initial concentration of 12.5 mM iron (or 687.5 mg/l as iron) in each catalyst. Exactly 120 ml of the catalyst solution was introduced at the top and allowed to permeate through the depth of the column. One column in each pair received acidified iron (II) catalyst as influent, while the second column in each pair received the modified Fenton's catalyst (ISOTEC^{SM} Cat 4260) as influent. The eluent collected at the base was analyzed for residual iron concentration (using the orthophenanthroline spectrophotometric method) and final pH value. Results for each column pair were compared to evaluate the sorption and mobility characteristics of each catalyst.

Results and Discussion

Results of the sorption experiments have been plotted in Exhibits 1 and 2. Exhibit 1 shows iron adsorption as a function of column depth for both modified Fenton's catalyst as well as acidified iron (II) catalyst. Nearly 100 percent of iron in acidified iron (II) catalyst was adsorbed to the soil when passed through a 300 g column (or 20 cm column). In comparison, only 13.6 percent of iron present in modified Fenton's catalyst was adsorbed. As expected, the percent sorption for both catalysts increased with the depth of the columns. While this increase is marginal for modified Fenton's catalysts, it is steep for acidified iron (II) catalyst, indicating that the mobility of this catalyst is very limited when injected into an in-situ environment. Using the concentration of residual iron in the eluent as the criteria, it is evident that modified Fenton's catalysts are at least 5 to 6 times more mobile than acidified iron (II) catalyst.
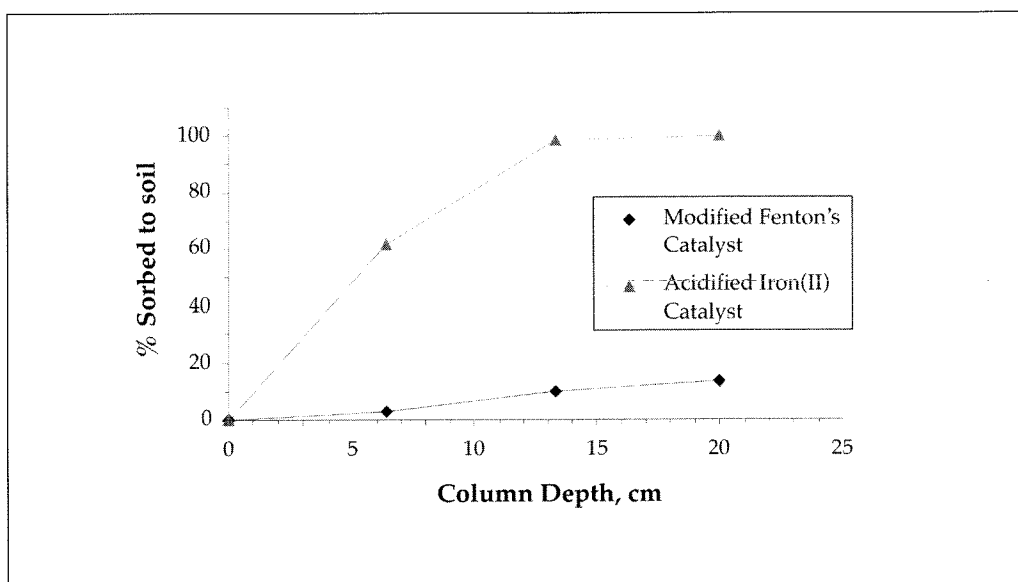

Exhibit 1. Modified Fenton's vs. conventional catalyst sorption in soil columns.

Exhibit 2 shows comparison of pH variation of the catalytic reagents with percentage of iron remaining in eluent plotted as a function of the column depths. The plot demonstrates a clear buffering effect of the soil on the injected catalysts as they permeate through the soil column. The pH of the acidified iron (II) catalyst gradually increased from its low values toward the pH range 4.75 to 5.5, whereas the near-neutral pH of the modified Fenton's catalyst gradually converged toward the pH range of 5 to 5.5 as the column depth increased. This increase in the pH of the acidified iron (II) catalyst significantly contributed to the increased adsorption of iron to the soil through precipitation at high pH values, as is evident in Exhibit 2. The chelates present within the modified Fenton's catalyst have a greater affinity toward iron compared with the native soil and, hence, minimized iron loss through adsorption during the permeation process. Therefore, as shown in Exhibit 2, the majority of iron introduced as modified Fenton's catalyst at the top of the column remained in solution even after permeating through the entire soil-column depth and, hence, was still available to promote effective reaction at a high pH. The soil column results confirmed the potential of the modified Fenton's process for effective in-situ field application.

FIELD CASE STUDY

The subject site located in northeast Florida consisted of a former dry-cleaning facility that is believed to have released chlorinated solvents into the subsurface from past operations. A laboratory treatability study was initially conducted to evaluate the effectiveness of the modified Fenton's process and estimate requirements for initial reagent volume for field application. Following a successful treatability study, a field-scale treatment program was implemented to reduce the overall chlorinated VOC
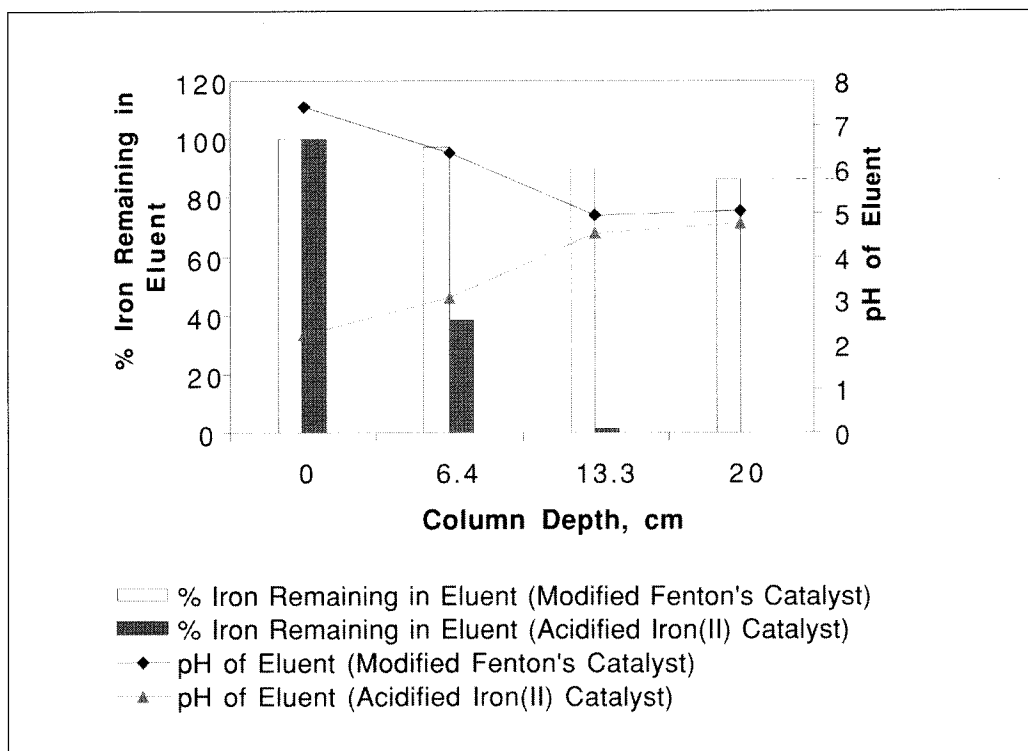

Exhibit 2. Modified Fenton's vs. conventional catalyst—comparison of pH variation.

contamination in the subsurface aquifer. The radial extent of influence was monitored via fluctuations in measured field parameters including iron, hydrogen peroxide, pH, and total dissolved solids (TDS). These measurements were conducted every day prior to initiating injection activities.

Site Characteristics

The primary contaminants of concern at the site are chlorinated VOCs, including *cis*-1,2-dichloroethene (*cis*-DCE), trichloroethene (TCE), *trans*-1,2-dichloroethene (*trans*-DCE), tetrachloroethene (PCE), and vinyl chloride (VC). The levels of total VOCs were recently found in excess of 1,850 µg/l within the treatment program's target area. A site map showing injection and monitoring point locations is presented in Exhibit 3.

The general subsurface lithology at the site consists of fine sands. Depth to groundwater is approximately 3 feet below grade with the groundwater flowing in an easterly direction (toward the building envelope). The hydraulic conductivity of the aquifer at the site is unknown, but a nearby property has a calculated conductivity of 1.62×10^{-4} feet/sec (14 feet/day). The contaminant zone of the aquifer is found at the 3-to-20-feet aquifer interval, with majority of contamination detected at the 10-to-12-feet depth interval.
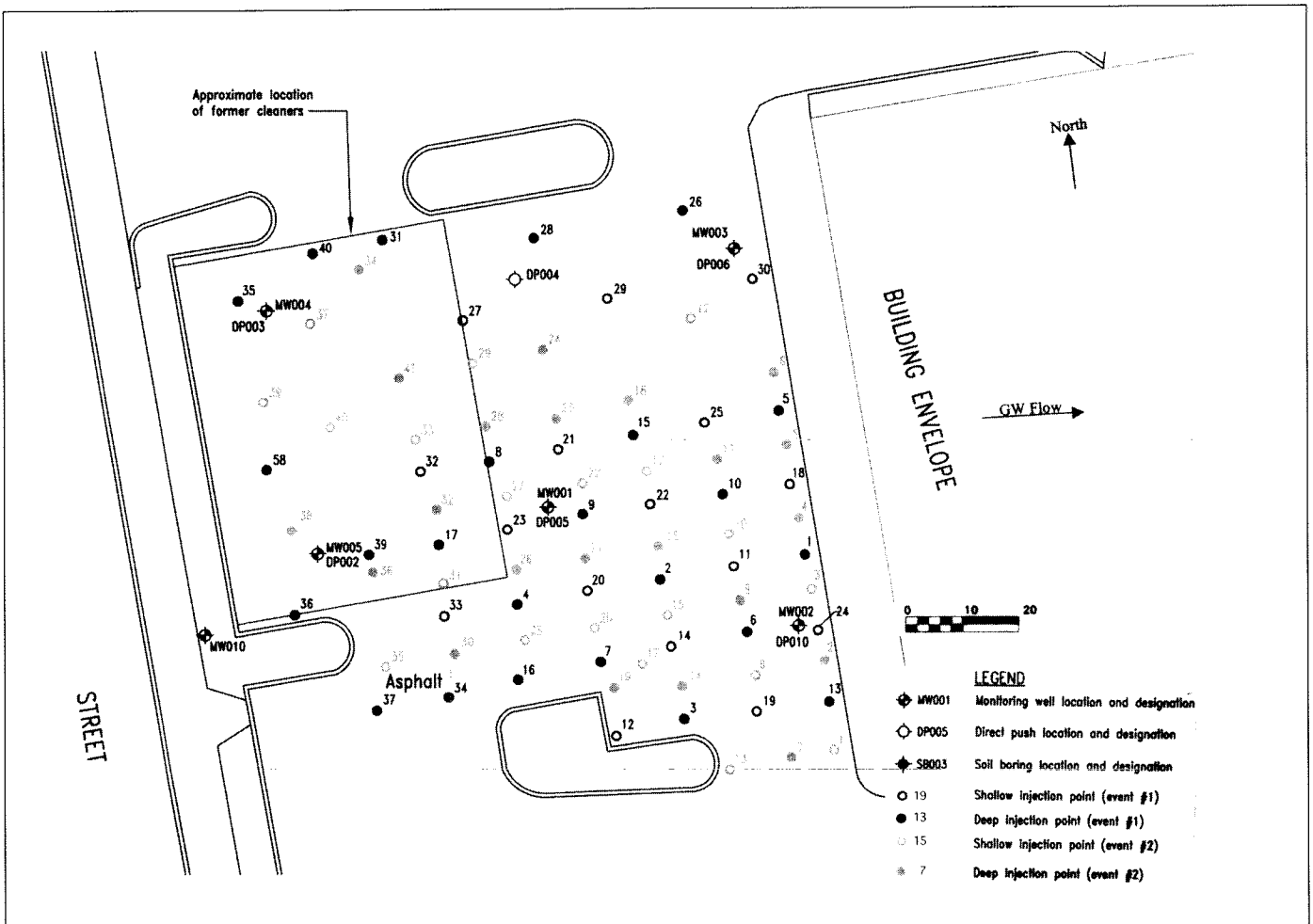

Exhibit 3. Site map showing injection and monitoring point locations.

Laboratory Treatability Experiments

Contaminant treatability experiments were conducted on soil-slurry and groundwater samples collected from the most contaminated area of the subject site (MW001 and vicinity). While the soil-slurry experiments were conducted to evaluate matrix effects, comparative groundwater experiments were conducted to evaluate VOC treatment under pristine conditions (i.e., without soil effects). Groundwater experiments were conducted in VOC-tight 140 ml reaction vessels, which were sealed with aluminum caps containing rubber septa. Soil-slurry experiments were conducted in VOC-tight 120 ml reaction vessels, which were sealed with screw-top caps containing Teflon septa. Modified Fenton's catalytic reagent and stabilized hydrogen peroxide were sequentially introduced as separate doses into the reaction vessels using syringes. Each treatment dose consisted of a concentration and volume of reagents that produced 1.60 mM as iron and 120 mM as H_2O_2. Excess H_2O_2 was mainly introduced to overcome the competing effects of TOC and transition metal catalysts that occurred naturally in the subject soil. The soil TOC was determined to be at 13,800 mg/kg, iron at 923 mg/kg, and manganese at 16.1 mg/kg in the soil tested. One of the reaction vials was initially

Matrix	Groundwater Test			Soil-Slurry Test		
Sample	Control	Treated #1	Treated #2	Control	Treated #1	Treated #2
Catalyst Used	None	Modified Fenton's	Modified Fenton's	None	Modified Fenton's	Modified Fenton's
Oxidant Used	None	Stab. H_2O_2	Stab. H_2O_2	None	Stab. H_2O_2	Stab. H_2O_2
No. of Treatment Doses	0	1	2	0	1	2
VOC (Units)	µg/l	µg/l	µg/l	µg/kg	µg/kg	µg/kg
trans-DCE	43	ND < 0.28	ND < 0.28	ND < 35.7	ND < 14.5	ND < 14
cis-DCE	1700	ND < 0.17	ND < 0.17	386	10.6 J	ND < 14
PCE	ND < 4.4	ND < 0.22	ND < 0.22	24.1 J	31.7	24.1
TCE	140	ND < 0.19	ND < 0.19	52.5	8.6 J	4.41 J
VC	ND < 3.8	ND < 0.19	ND < 0.19	ND < 35.7	ND < 14.5	ND < 14
Total target VOCs	**1,883**	**ND**	**ND**	**481.1 J**	**54.82**	**28.51 J**
Total TICs	ND	10.4	6.7	ND	ND	15.7
Percent Reduction (Total target VOCs)	——	**> 99.9%**	**> 99.9%**	——	**88.6%**	**94.1%**
Final pH of Groundwater	**6.25**	**5.78**	**5.84**	**6.95**	**6.19**	**6.28**

Note:

ND = Analyzed for but not detected at the method detection limit (MDL) indicated by the number following "<" sign.

VOC = Volatile organic compound.

TICs = Tentatively identified compounds or nontarget compounds (includes only the top-ten compounds or peaks detected in a forward library search).

µg/L = micrograms per liter, µg/kg = micrograms per kilogram.

Percent reduction calculations are relative to control sample and assume ND value as zero.

Exhibit 4. Case study—results of soil-slurry and groundwater contaminant treatability experiments.

isolated to serve as a control sample and received equivalent doses of distilled water to compensate for the reagent volumes injected. The reaction vessels were left undisturbed for at least 24 hours or until such time that the peroxide was completely consumed. Each reaction vessel was spiked with a drop of catalase to decompose any residual peroxide. All samples were analyzed for volatile organic compounds by EPA Method 8260/624.

The results of the treatability study performed on contaminated groundwater and soil slurry procured from the subject site are presented in Exhibit 4. The results indicate that all targeted VOCs were reduced to nondetectable (ND) levels after only one treatment (greater than 99.9 percent reduction) in the groundwater test when compared with the control sample. The results of the soil-slurry test indicated up to a 94 percent reduction of targeted VOCs in the slurry sample after two treatment doses when compared with the control sample.

The study results were used to design a field-scale application of the modified Fenton's process for the site from which the study samples were collected. Even though these results provided only minimal information about the site-specific effectiveness of the process, they demonstrated the effectiveness of the modified Fenton's reagents toward oxidation of chlorinated contaminants of concern under controlled conditions. Also, when combined with the data on mobility and sorption characteristics presented in Exhibits 1 and 2 (tested on an organic soil from New Jersey as opposed to actual soils obtained from this site for contaminant treatability), the contaminant treatability results demonstrated the enormous potential of modified Fenton's processes toward in-situ field application.

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Injection Activities

The injection activities of the field treatment program were conducted over two 4-day events (Phase I and Phase II) spread approximately one month apart. During Phase I, a total of 20 deep injection points and 20 shallow injection points were installed using direct-push (DP) technology to encompass the delineated area of the plume (Exhibit 3). The same number of injection points was also used during Phase II; however, the locations differed as shown in Exhibit 3. The injection points were installed at two separate depths (8 to 12 ft bgs for the shallow and 12 to 16 ft bgs for the deep) throughout the treatment area to treat the entire target zone of the aquifer. The injection points were spaced no more than 25 feet from one another at each of the two separate depths. Each DP point consisted of a 1.25-inch ID stainless steel casing driven into the subsurface via a DP rig. The casing end contained an expendable stainless steel tip. Solid sections of 4-foot casing were advanced to the desired treatment depth (approximately 12 feet bgs for the shallow points or 16 feet bgs for deep points). Once the desired depth was reached, a 4-foot section was withdrawn, leaving a 4-foot open borehole for injection. All DP injection points were grouted using bentonite and cement after the daily field activities were completed. By utilizing DP injection techniques, each injection point could be selected based on previous groundwater sampling data to target the contaminant source area. A typical process block diagram for the injection system used at the site is provided as Exhibit 5. Connections to the injection point were made via an assembly of diaphragm pumps, reinforced PVC hoses, and valves. Reaction and injection pressures were monitored via pressure gauges installed both at the pump head as well as
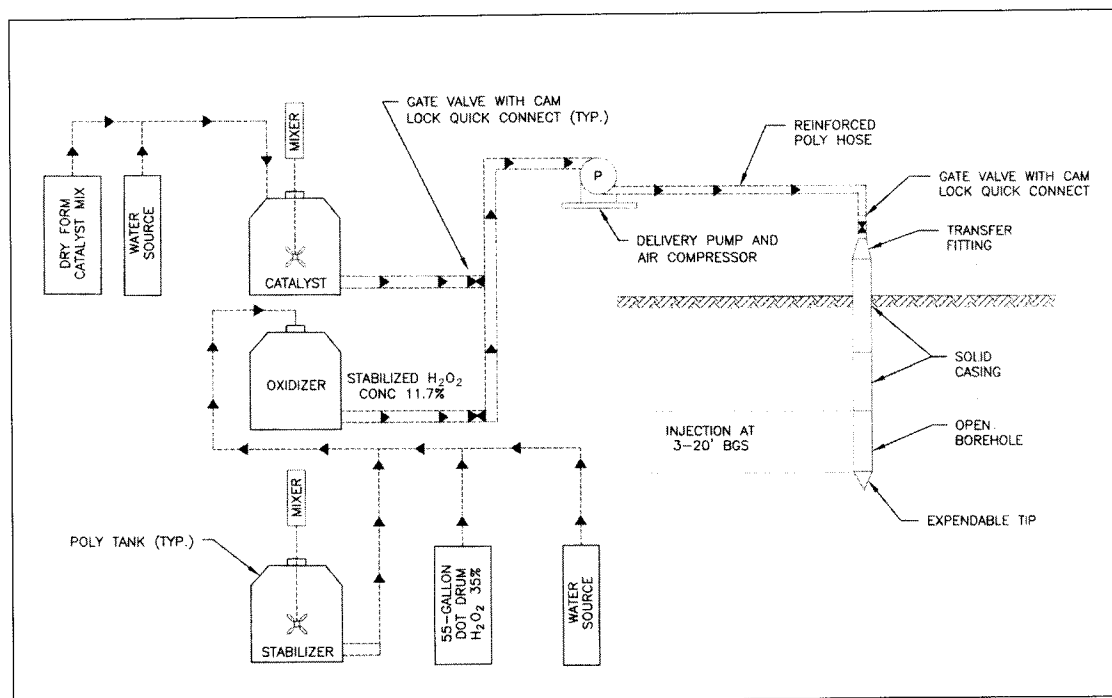
Exhibit 5. Typical ISOTEC^{SM} process block diagram.

the injection-point head. A relief valve was installed at the top of each injection point to relieve excess reaction pressures and off-gases, when necessary. Pressures generated during the treatment program fluctuated between 15 and 40 psi.

Approximately 360 gallons of modified Fenton's catalyst and stabilized 11.7 percent hydrogen peroxide (in a 1:2 ratio by volume) were injected into each of the designated points with associated average catalyst and oxidizer injection flow rates at 10 gallons per minute (gpm). Groundwater samples were collected from eight existing monitoring wells prior to injection to provide baseline VOC data. In addition, sampling was performed in between the two phases, and approximately one month after Phase II at the same locations.

Results and Discussion

Cumulative results of baseline and post-treatment contaminant concentrations detected in all the monitor wells have been plotted in Exhibit 6. When compared with the baseline samples collected, the groundwater analytical results collected after the first and second injection events showed an average 72 percent and 90 percent decrease in total site-wide VOC concentrations, respectively. Site-wide cumulative VOC concentration in groundwater has been substantially reduced from 3,506 µg/l to 363 µg/l after two injection events.

The most contaminated location (i.e., MW001), where total VOCs decreased from 2,888 µg/l to 258.9 µg/l, showed greater than 91 percent reduction. The percent reduction of all VOCs in groundwater improved with each treatment event. Site-wide primary VOCs consisting of *cis*-DCE, *trans*-DCE, PCE, TCE, and VC were reduced by 91 percent, 72 percent, 99.9 percent, 96 percent, and 51 percent, respectively, following the treatment program. Downgradient monitoring wells east of the building envelope
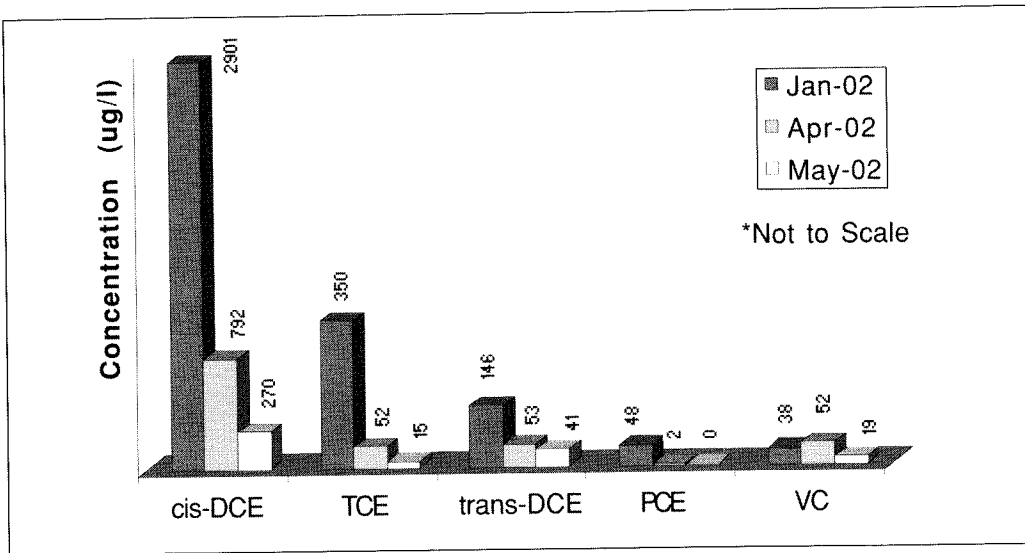
Concentration (ug/l)

Jan-02
Apr-02
May-02

*Not to Scale

2901, 792, 270 — cis-DCE
350, 52, 15 — TCE
146, 53, 41 — trans-DCE
48, 2, 0 — PCE
38, 52, 19 — VC

Exhibit 6. Pre- vs. post-treatment results of treatment program. The bars represent the contaminant concentrations. The treatment program Phase I injection activities were conducted in March 2002 and Phase II injection activities were conducted in April 2002.

(not shown) indicated total VOC reductions of greater than 99 percent to nondetect concentrations. Exhibit 7 presents fluctuation in pH data during the treatment program. As is evident from the data, although fluctuations in pH occurred during the course of the treatment program depending on the concentration of reagent influencing a given well, the final pH remained more or less within the desired native soil range of 5 to 7. These data demonstrate that effective VOC reduction can be achieved under native soil pH conditions using modified Fenton's reagent.

During the injection activities, visual observation of effervescent water bubbling and rise in water-level elevations were observed in all the monitoring points in the target treatment area (including MW001 and MW002), indicating that the reagents had
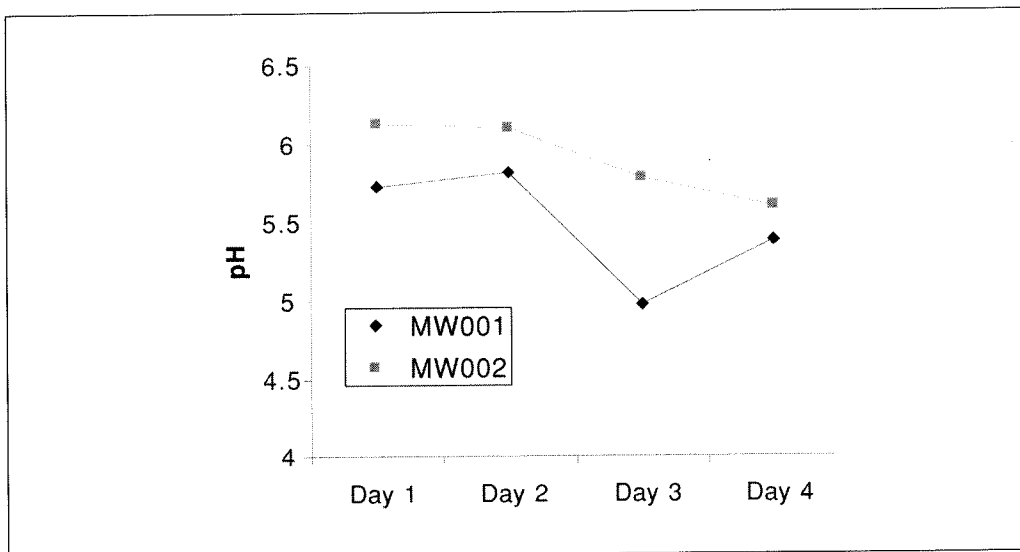

pH

MW001
MW002

Day 1   Day 2   Day 3   Day 4

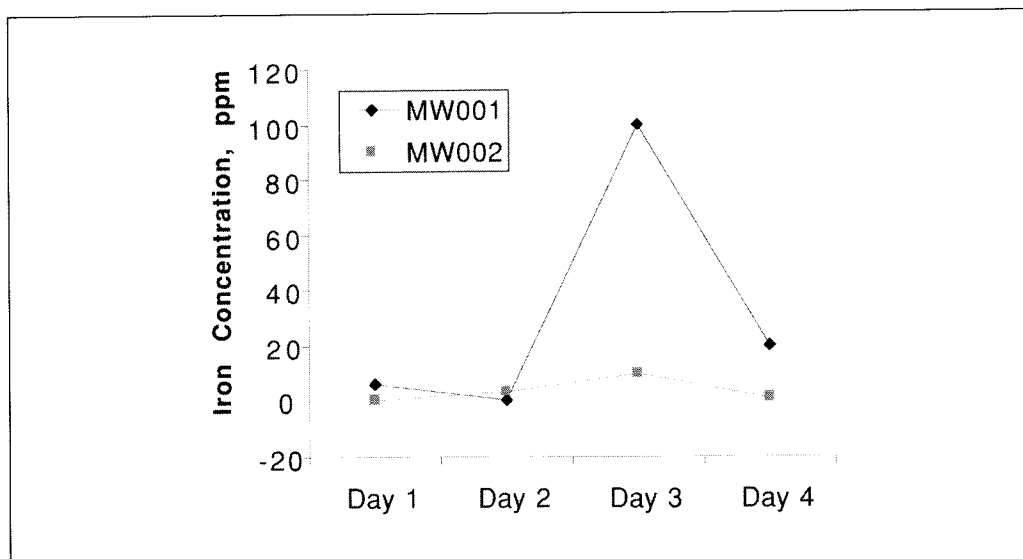**Exhibit 7.** Fluctuation in pH during treatment program.

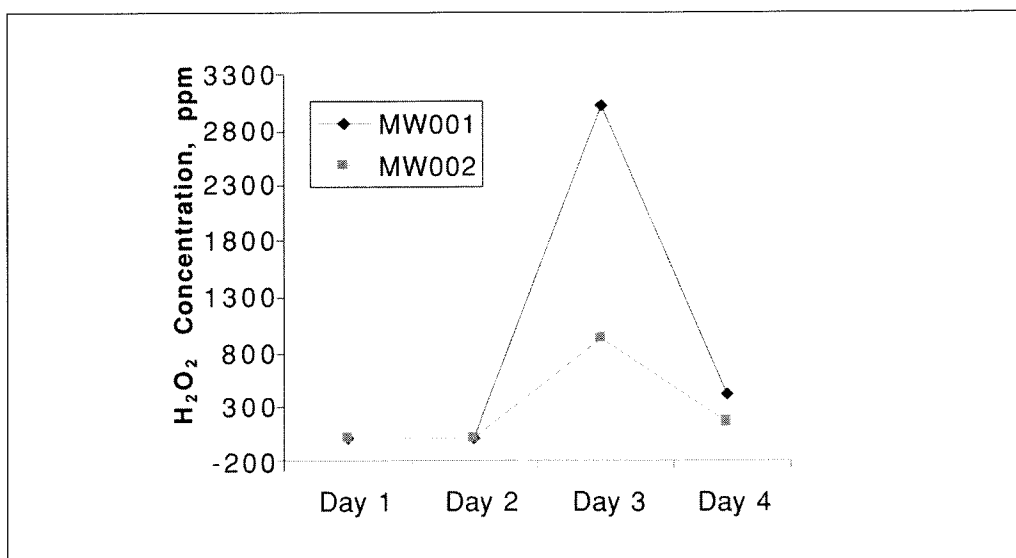**Exhibit 8.** Fluctuation in iron concentration during treatment program.

Exhibit 9. Fluctuation in H_2O_2 concentration during treatment program.

migrated to areas where monitoring points were located. Furthermore, the field monitoring data (Exhibits 8 and 9) collected from MW001 and MW002 confirmed significant increases in both iron and hydrogen peroxide concentrations during the course of injections. The concentration of TDS increased in a majority of the wells, likely due to the presence of high concentrations of dissolved iron, indicating influence of reagents injected in the vicinity. Based on the location of the monitoring points relative to the injection points, a conservative minimum radial influence of approximately 10 to 12 feet was estimated for the site.

SUMMARY AND CONCLUSIONS

In-situ application of the Fenton's reagent in its conventional form is impractical due to the acidic pH (i.e., pH 3 to 4) requirement, and limited mobility and sorption characteristics of the catalyst. Modified Fenton's processes are designed to mitigate the effects of natural processes such as pH buffering, soil adsorption, iron precipitation, and peroxide decomposition that occur when reagents are introduced into the subsurface. Laboratory soil-column experiments were used to compare the sorption and mobility characteristics of the modified Fenton's catalysts with conventional Fenton's catalysts, such as acidified iron (II). Overall, the results demonstrated that nearly 100 percent of iron present in a conventional catalyst was adsorbed when passed through a soil column packed with organic soil. On the contrary, only 13.6 percent of iron present as modified Fenton's catalyst was adsorbed. The acidic pH of conventional catalysts was quickly buffered to the native soil pH range, where iron does not stay dissolved, thus rendering conventional Fenton's reagent ineffective. Modified Fenton's catalysts have chelating compounds that have a greater affinity for iron compared with native soil even under native pH conditions, thereby maintaining iron in a dissolved form. Hence, free-radical generation takes place over a wide pH range.

Field-scale demonstration of the modified Fenton's process was conducted at a former dry-cleaning facility in northeast Florida. Following a successful laboratory treatability study, a series of DP injection points were installed in a grid fashion to introduce the modified Fenton's reagent into the subsurface. Results of the treatment program indicated a 72 percent reduction in total chlorinated VOCs, following the first injection event, which then increased to 90 percent reduction following the second injection event.

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Prasad K. Kakarla, P.E., is the technical director of In-Situ Oxidative Technologies Inc. He is a registered professional engineer in the state of New Jersey. He is an environmental engineer with research interests in the in-situ application of chemical oxidation for soil and groundwater remediation and has over eight years experience in the laboratory and field implementation of various chemical oxidation systems.

Thomas Andrews, P.E., is the vice president of In-Situ Oxidative Technologies Inc. He is a registered professional engineer in the states of New Jersey and New York and is experienced in the design and implementation of soil and groundwater remediation systems, stormwater management, hydraulics, wastewater treatment, and public water supply.

Richard S. Greenberg, Ph.D., is a consultant for In-Situ Oxidative Technologies Inc. He is a chemist with 18 years of experience in the environmental and chemical industries, holds multiple patents, and serves on numerous government/business advisory committees that help shape environmental policy.

David S. Zervas, president of In-Situ Oxidative Technologies Inc., has overall responsibility for achieving the technology development goals and long-term business objectives of ISOTEC. Prior to his association with the company, Mr. Zervas served as regional manager for an environmental consulting and remediation firm. He also has over ten years of prior professional experience with the New Jersey Department of Environmental Protection (NJDEP). Mr. Zervas was involved in various enforcement programs with the NJDEP, including ECRA, RCRA, DOD facilities, and Superfund.