In Situ Chemical Oxidation of MGP Residuals

Field Demonstration Report

1015411

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Technical Update, August 2007

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PRODUCT DESCRIPTION

Bench-scale testing and a field demonstration were performed to determine the technical feasibility, economics, and limitations of using activated persulfate for *in situ* chemical oxidation (ISCO) of manufactured gas plant (MGP) residuals. Based on the testing performed and available industry knowledge, the general principles of applying ISCO as an alternative to dig and haul have been incorporated into this project.

Results & Findings

Activated persulfate is a useful oxidant for application at MGP sites because of its stability and aggressiveness in the subsurface. The stability and persistence of the oxidant dictates its ability to be transported in the subsurface at sustained concentrations that are needed to treat low-solubility MGP contaminants. Typical contaminants of concern (COCs) at MGP sites include polycyclic aromatic hydrocarbons (PAHs), aromatic hydrocarbons (benzene, toluene, ethylbenzene, and xylenes [BTEX]), and total petroleum hydrocarbons (TPH).

Greater than 90 percent of COCs were reduced after multiple applications of persulfate during bench-scale testing. A single application of alkaline-activated persulfate was selected for the field demonstration. This field application only targeted a portion of COCs considered to be readily oxidizable. COCs were reduced by 40 and 60 percent in the one field application at the demonstration site.

In April 2006, an alkaline-activated persulfate application was initiated in a predetermined target treatment volume within the Laurel Street former MGP site in Poughkeepsie, New York. Soil samples were collected before and after the single activated persulfate application. Data indicated reductions in the average total PAH and TPH concentrations of approximately 55 and 68 percent, respectively, whereas the average total BTEX concentration increased by approximately 4 percent.

An additional evaluation of the data indicated reductions in the mass of PAHs (ranging from 49 to 63 percent) and TPH (ranging from 63 to 75 percent). There was effectively little to no change to the mass of BTEX compounds (-2 percent to 1 percent mass reduction). The measured reductions met the treatment expectations as originally estimated based on bench-scale testing conducted on the site soils. The data also demonstrated that leaching of COCs from the treated site soils decreased by 62 percent for PAHs and 26 percent for BTEX compounds, relative to untreated site soils.

Challenges & Objective(s)

The overall objective of this project was to provide MGP site managers with sufficient information on the technical feasibility, economics, and limitations of applying ISCO when using activated persulfate for MGP residuals. Several subsurface characteristics are critical to the application of ISCO. These include soil type, hydraulic conductivity, and soil heterogeneity. The amount of oxidant exerted, the groundwater flow, and the site's geochemistry also are important. Expectations and remedial goals also were critical to the success of this project. Remedial goals included expected decreases in nonaqueous phase liquid (NAPL) and contaminant concentration in groundwater. As with any *in situ* treatment technology, the more stringent the cleanup goal, the more difficult and expensive it is to achieve the goal using ISCO.

Applications, Values & Use

One specific objective of this project was to develop some general principles to guide managers of MGP sites when considering using ISCO, and specifically activated persulfate. Site managers seeking site-specific cleanup objectives may find ISCO to be a cost-effective remedial alternative. The project illustrates how ISCO technologies have the potential to treat soils contaminated with MGP residuals within a specific concentration range. ISCO treatment costs are site dependent, but may typically vary from $100 to $500 per cubic yard (in year 2006). This project also demonstrated that activated persulfate can be applied safely at MGP sites.

EPRI Perspective

Results of this project will provide site managers with an understanding of how to apply site-specific cleanup objectives using ISCO. This report describes site conditions where ISCO may be a cost-effective remedial alternative to dig and haul operations. This project was undertaken to determine whether persulfate could be a cost-effective remedial technology for MGP-impacted soils and groundwater. This project also focused on evaluating persulfate as a stable and persistent oxidant. Sustained concentrations of persulfate are needed to treat low-solubility MGP constituents. Results of this study show that persulfate can effectively reduce MGP contaminants to certain concentrations. However, this project did reveal many limitations of using persulfate on source coal tar material. A site manager seeking to use ISCO is urged to have a very good understanding of a site's geology, lithology, groundwater chemistry, and source contamination levels before applying ISCO as a holistic remedial technology. Persulfate as an ISCO remedy is not well documented in the literature for use at MGP sites. This paper serves to fill a large gap in the literature.

Approach

This ISCO demonstration focused on using persulfate as an oxidant. Iron- and alkaline-activated persulfate techniques were evaluated for the remediation of TPH, PAHs, and BTEX compounds found at MGP sites. This work involved bench-scale testing of soils from two former MGP sites followed by a field demonstration using alkaline-activated persulfate at one former MGP site.

Keywords

PAHs MGP Fenton's reagent In situ chemical oxidation (ISCO)
Persulfate

ABSTRACT

Limited solutions are available for cost-effective remediation of manufactured gas plant (MGP) sites. Remedial measures typically involve nonaqueous phase liquid (NAPL) removal via pumping from large diameter, closely spaced wells and subsequent excavation and disposal (dig and haul) of shallow, impacted soils. Due to surface impediments or the inability at some sites to dig and haul, there is a demand for an *in situ* remedial technology for MGP residuals that comply with regulatory goals and standards. This technical update provides details on bench-scale testing and an *in situ* chemical oxidation (ISCO) demonstration using activated persulfate and demonstrates the technical feasibility, economics, and limitations of ISCO persulfate. One project objective was to develop general principles to guide managers of MGP sites when considering the application of ISCO as a remedial action alternative. This guidance is intended to help site managers understand what site-specific cleanup objectives ISCO can achieve and for which site conditions ISCO may be a cost-effective alternative.

ACRONYMS

AEHS	Association for Environmental Health and Sciences
BBL-ARCADIS	BBL-ARCADIS-An Arcadis Company
bgs	below ground surface
BTEX	benzene, toluene, ethylbenzene, and xylenes
ºC	degrees Celsius
CHGE	Central Hudson Gas & Electric Corporation
CHP	catalyzed hydrogen peroxide, commonly known as Fenton's Reagent
cm/sec	centimeters per second
COC	contaminant of concern
COD	chemical oxygen demand
EPA	Environmental Protection Agency
EPRI	Electric Power Research Institute
ft/day	feet per day
ft MSL	feet above mean sea level
gpm	gallons per minute
g/L	grams per Liter
H_2O_2	hydrogen peroxide
ISCO	*in situ* chemical oxidation
LNAPL	light non-aqueous phase liquid
mg/Kg	milligrams per Kilogram
mg/L	milligrams per Liter
mV	milliVolt
MGP	manufactured gas plant
mL	milliLiter
NaOH	sodium hydroxide
NAPL	non-aqueous phase liquid
NYSDOT	New York State Department of Transportation

ORP	oxidation-reduction potential
ORTs	Oxidation and Reduction Technologies Conference
PAH	polycyclic aromatic hydrocarbon
POD	Portable Oxidant Delivery
SPLP	Synthetic Precipitation Leaching Procedure
TarGOST®	Tar-specific Green Optical Screening Tool™
TOC	total organic carbon
TPH	total petroleum hydrocarbons
VOC	volatile organic compound
XDD	XDD, LLC

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- Central Hudson Gas and Electric Corporation provided a location for the field demonstration of this technology; and,
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INTRODUCTION

This technical update report provides details on bench-scale testing and an *in situ* chemical oxidation (ISCO) demonstration using activated persulfate. The research was conducted at the Central Hudson Gas & Electric Corporation (CHGE) former Laurel Street MGP site in Poughkeepsie, New York. One of the project objective was to develop some general principles to guide managers of MGP sites when considering the application of ISCO as a remedial action alternative. The project also sought to demonstrate the technical feasibility, economics and limitations of ISCO persulfate.

The project evaluated Klozür™ Activated Persulfate[1] (Klozür™) as one potential cost-effective oxidant for treating MGP-impacted soils and groundwater. Activated persulfate was selected for the demonstration because it is considered to be a promising and flexible oxidant for application at MGP sites as a result of its stability and aggressiveness in the subsurface. It is the stability and persistence of the oxidant that dictates its ability to be transported in the subsurface and to sustain concentrations that are needed to treat low solubility MGP constituents.

Contamination at a typical MGP site includes oil and coal tar found as free [non-aqueous phase liquid (NAPL)], residual, sorbed and dissolved phases in the subsurface. Analysis of soil or groundwater samples for total petroleum hydrocarbons (TPH) provides a collective measure of oily substances present in the sample. These oily substances measured by TPH include polycyclic aromatic hydrocarbons (PAHs) and benzene, toluene, ethylbenzene and xylenes (BTEX) along with other petroleum hydrocarbons.

Problem Statement

Limited solutions are available for cost-effective remediation of MGP sites. Remedial measures typically involve NAPL removal via pumping from large diameter, closely spaced wells; and subsequent excavation and disposal (dig and haul) of shallow, impacted soils.

Due to surface impediments or the inability at some sites to dig and haul, there is a demand for an *in situ* remedial technology for MGP residuals that can comply with regulatory goals and standards.

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[1] Klozür™ is a trademark of FMC Corporation; FMC donated the Klozür™ Activated Persulfate for this field demonstration.

Scope of Work/Objectives

This ISCO demonstration focused on persulfate, and evaluated the remediation of an MGP site by activated persulfate. Catalyzed hydrogen peroxide (CHP- also known as Fenton's reagent) and activated persulfate are two of the most powerful oxidants available for application at MGP sites. The higher level of stability, low level of potential health and safety issues, and ease of application supports activated persulfate as a good oxidant option for MGP sites. Stability and persistence allows persulfate transport to and treatment of inaccessible impacted areas. The number of oxidant applications and injection point spacing can be minimized by using persulfate. Persulfate solution can be recirculated or otherwise applied with lower frequency to target areas at sustained concentrations for extended contact times needed to treat low solubility MGP constituents.

The rate of desorption of PAHs from soils is one of the most important factors in determining the application design of an ISCO technology such as persulfate. Certain soil compositions allow the COCs to be readily available for oxidation requiring only one or two applications of an oxidant and a relatively short oxidant contact time (i.e., a few days) to achieve remedial objectives. Other soil compositions with more clay for example, permit only slow desorption of the COCs requiring longer contact time (i.e., 30 to 60 days) and multiple applications of the oxidant.

Two sites were evaluated for the ISCO demonstration: the North Water Street MGP site and the Laurel Street MGP site. Both sites are located in Poughkeepsie, New York. Bench scale studies were conducted on soil and groundwater from both sites to determine the goals for the field pilot demonstration. The bench testing results were used in developing the field application approach.

The field application was performed at the Laurel Street MGP site, and the demonstration results were used to evaluate the following secondary objectives:

- Were the endpoint expectations met for this field demonstration?
- Did the ISCO application affect the leachability potential of COCs from the soils?
- Can oxidant-loading criteria be developed so that it is transferable across multiple sites?
- What are the general value benefits to using an activated persulfate application at an MGP site?
- Strong oxidants can be corrosive and can produce heat and off-gases. This requires additional health and safety considerations and may preclude usage in certain areas. Can activated persulfate be applied safely?

And,

- How did the application approach and subsurface heterogeneities affect the treatment effectiveness?

General guidance principles are developed for site managers when considering the application of ISCO. The guidance principles are based on the information developed as part of this demonstration project and on experiences gained by XDD and others in the application of ISCO at both MGP and non-MGP sites. This guidance is intended to help site managers understand what site-specific cleanup objectives ISCO can achieve and for which site conditions ISCO may be a cost-effective alternative.

Report Contents

Section 2 describes persulfate chemistry and activation techniques. Section 3 summarizes characteristics of the two sites evaluated for the ISCO demonstration and provides the rationale for selection of the Laurel Street site for the field application. Section 4 summarizes the bench-scale testing work and discusses the testing results. Section 5 describes the demonstration fieldwork and provides sampling results and data evaluation. Section 6 provides general guidance for managers of MGP sites when considering the application of ISCO. Section 7 presents summary and conclusions of the demonstration.

2

CHEMISTRY OF ACTIVATED PERSULFATE

ISCO is a general term for several different technologies that degrade contaminants via oxidative chemical reactions. The most common ISCO technologies include permanganate, activated sodium persulfate, catalyzed hydrogen peroxide (CHP- also known as Fenton's reagent), and ozone. Brief descriptions of these technologies with respect to their application for MGP residuals are presented in Section 6. This section provides details on the chemistry associated with the activated sodium persulfate reactions.

Sodium persulfate, sometimes referred to as sodium peroxydisulfate, is a key component of many industrial processes and commercial products. For example, sodium persulfate has been used for decades as an oxidant in the analysis of organic carbon in aqueous samples, and in water and wastewater treatment. Over the last several years persulfate has been considered for *in situ* remediation applications. One of the first applications was performed in the mid-west in 1998 at a site contaminated with chlorinated solvents.

The persulfate anion ($S_2O_8^{2-}$) is the most powerful oxidant of the peroxygen family of compounds, and is among the strongest oxidants commonly used for water and wastewater treatment. The persulfate anion can be activated by several methods to form the sulfate radical ($SO_4\bullet$), a powerful and relatively non-selective oxidant with a standard reduction potential of 2.6 Volts (Neta et al., 1977). While activation to form the sulfate radical exists as common knowledge within the industry, it is fairly well established that the chemistry of persulfate activation is more complex and that the potential exists to produce a number of different radicals that can aggressively degrade a wide suite of target compounds. Activated persulfate in a batch reactor system is observed to first react with the readily available or easily desorbed compounds, and then slowly reacts with more recalcitrant or more highly sorbed compounds.

The activation methods for persulfate include heat, reaction with a reduced transition metal such as ferrous iron, and auto-decomposition of the persulfate under slightly acidic or alkaline conditions.

This project evaluated two of the activation methods: iron activation and alkaline activation. The third, heat activation, was not evaluated because of concerns about the mobilization of MGP NAPL from the test zone and the potential costs to apply the heat over large volumes of soil.

Iron-Activated Persulfate

Iron-activated persulfate (Liang et al., 2004) is based on the stoichiometric reaction between persulfate and ferrous iron as shown below:

$$Fe^{2+} + S_2O_8{}^{2-} \rightarrow Fe^{3+} + SO_4{}^{2-} + SO-_4 \bullet$$

In this activation method only one of the two available sulfate molecules becomes a radical. Iron typically has a very low solubility at neutral pH. Chelates are generally used to keep the iron in solution (Sun and Pignatello, 1992) and, thereby activate the persulfate (Liang et al., 2004). Maintaining the persulfate and iron reagents together *in situ* to propagate the reactions requires appropriate design of the application approach.

Alkaline-Activated Persulfate

Several key differences in the chemistry of iron and alkaline activation, depending on site-specific conditions, can affect treatment of contaminated soils. Potential advantages of alkaline-activated persulfate include: the generation of two sulfate radicals per persulfate molecule (Ebina et al., 1983) and the generation of the hydroxyl radical. Anipsitakis and Dionysiou (2004) discusses options for an easier application approach to maintain the alkaline activation condition without the concern of the reagents not maintaining mixing in the subsurface; and minimize evolution of heat and gas.

The activation method is based on the auto-decomposition of persulfate under alkaline conditions, which is believed to cause the persulfate molecule to break at the O-O bond, resulting in the formation of two sulfate radicals:

$$S_2O_8{}^{2-} \rightarrow 2SO-_4 \bullet$$

Additional propagation reactions are possible after this initial step (DeLatt and Le, 2005; Block et al., 2004) including the probable formation of the hydroxyl radical, but current research has not yet definitively identified all of these reactions.

3

MGP SITES SELECTED FOR EVALUATION

Of the two CHGE former MGP facilities, the Laurel Street site, located in Poughkeepsie, New York was eventually selected for the field pilot test. Bench-scale testing work was however performed on soils obtained from both sites. The following subsections provide the background and hydrogeological data on both sites.

North Water Street Site

The North Water Street site (Figure 3-1) is bounded to the north by Dutchess Avenue, to the east by North Water Street and Amtrak railroad lines, to the south by an inactive elevated railroad bridge, and to the west by the Hudson River. To the north of the site lies a vacant lumberyard, and to the south lies property owned by CHGE that is used as an electric substation.

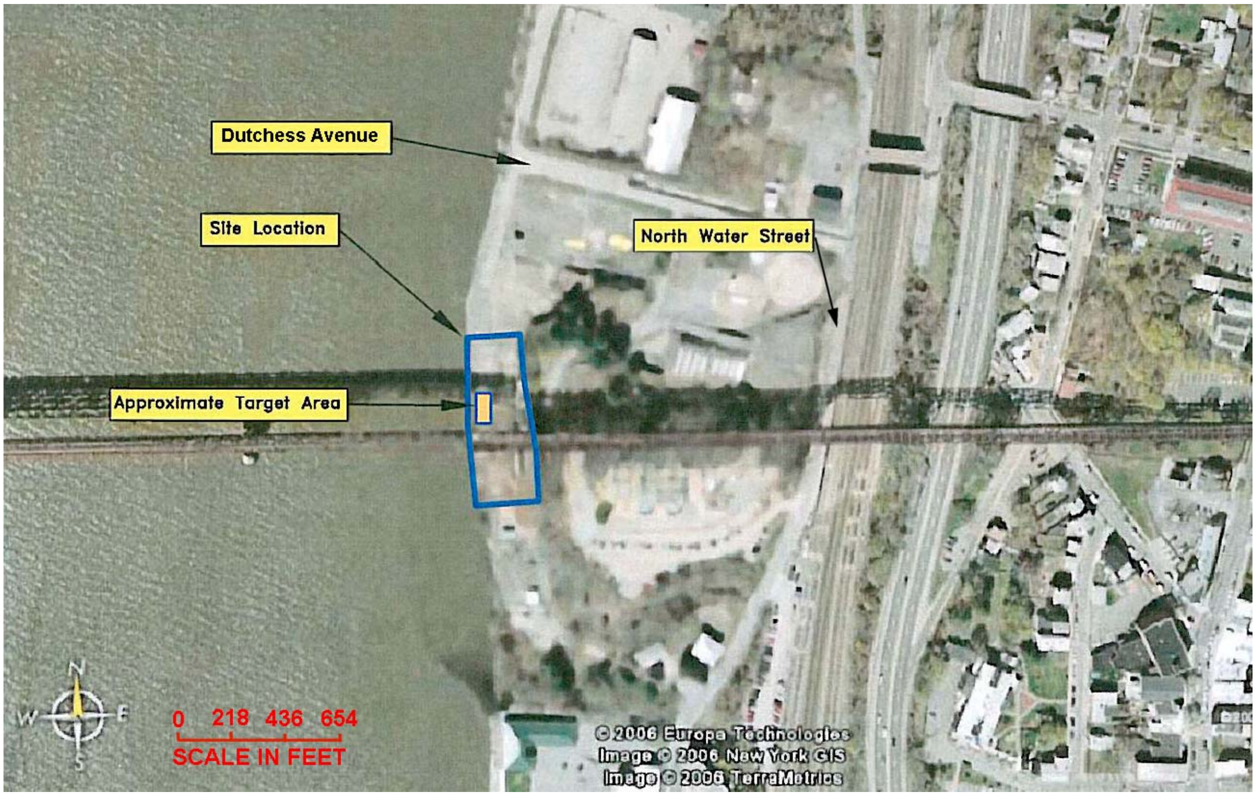

Figure 3-1
The North Water Street Site Location Map

The former North Water Street MGP produced carbureted water gas from 1911 to 1950. CHGE has owned the site since 1926. From 1950 to 1954, as the demand for manufactured gas decreased, the North Water Street MGP was used only for peak gas demands. By 1955, some of the gasification facilities and equipment were removed from the property and gas manufacturing was discontinued.

This two-acre property is surrounded by a fence, where CHGE currently operates a propane peaking plant and natural gas regulator station. Features associated with the propane operations include propane storage tanks, a high-pressure compressed air holder, and office/operations buildings. Most of the site is paved or covered by gravel.

Topographic relief at the site ranges from approximately four feet above mean sea level (feet MSL) along the river to approximately 63 feet MSL along North Water Street. A bedrock cliff of schist is located approximately 100 feet east of the river, creating upper (eastern) and lower (western) sections of the site. In the lower section of the site along the Hudson River, the bedrock is topped by an overburden that consists of fill underlain by shale gravel, silt and till. Silt and clay lenses and wood are present within both the fill and gravels/silts in the northern half of the lower section of the site. In addition, a lower 5- to 25-foot thick silt and clay unit is present between the gravels/silts and the bedrock in the northern half of the lower section of the site. Bedrock consists of schist, low-grade metamorphic shale and greywacke.

Groundwater is located between three to seven feet below ground surface (bgs), and is tidally influenced (i.e., a four feet water table fluctuation every six hours). While preliminary bench-scale testing results on the site soils appeared promising (as presented in Section 4), the tidal fluctuation across the proposed demonstration area raised concerns as to the site’s applicability for a limited field demonstration.

To evaluate the potential impacts of the tidal influence on the proposed oxidant injection, a series of hydraulic analyses were performed at the site to refine the understanding of the lateral groundwater travel in the proposed demonstration area as a result of the tidal fluctuations. The results of the hydraulic analyses suggested that the lateral groundwater flow in the demonstration area would not provide adequate contact time between the injected oxidant and the target soil volume. To evaluate the lateral groundwater velocity a tracer test was conducted in the demonstration area by injecting a slug of tracer into a well installed within the target soil volume and monitoring the decline in tracer concentration in the well over time to represent the contact of an oxidant with the target soils.

The results of the field tracer test demonstrated that the site hydraulics would result in rapid (i.e., less than two to four hours) sweeping of the oxidant from the target soil volume, not allowing sufficient contact time to achieve the project goals. To achieve the demonstration objectives in this area would have required a physical or hydraulic barrier to contain the water migration in the area. It was concluded that this test layout would not reflect a typical full-scale system design and application for this type of site. Further, alternatives to achieve the required hydraulic control were deemed too expensive for the available project budget. Therefore, based on the site hydraulics, with respect to implementation of the field pilot test, the former North Water Street site was not selected for the demonstration.

Laurel Street Site

The Laurel Street site (Figure 3-2) is located in a mixed commercial and residential area. Laurel Street to the north, former Gate Street to the east, a residence to the south along Grove Street, and the southbound lane of the Route 9 Arterial to the west bound the site. North of Laurel Street lays the Dutchess Beer Distributors Incorporated facilities, and further to the east and south lays a residential neighborhood. West of the Route 9 Arterial lies property used by the New York State Department of Transportation (NYSDOT) as a field office/staging area for Route 9 and other road repairs. The Hudson River lies approximately 1,500 feet west of the site.

Figure 3-2
The Laurel Street Site Location Map

The former Laurel Street MGP operated from circa 1875 to 1911. By 1919, the MGP facilities and equipment were removed from the Laurel Street site and relocated to another CHGE property. Both coal carbonization and carbureted water gas processes were used at the site during its operation.

This 1.5-acre property is open area with grass cover, brush, and trees over approximately two-thirds of the site with the northbound lane of the Route 9 Arterial covering the other third. Features at the site include a former steel tank along the eastern fence line of the Route 9 Arterial, former foundations, and scattered brick and building debris.

Topographic relief at the site ranges from approximately 80 to 90 feet MSL along the southern (higher) portion of the site to approximately 50 feet MSL along Laurel Street. Shallow site geology consists primarily of fill and silty sand material underlain by till and/or a clay/silt unit (this unit is observed only along the northern half of the property, closer to Laurel Street). Groundwater flows toward the northwest, and the depth to groundwater ranges from approximately seven to nine feet bgs. Results of hydraulic conductivity tests performed at two of the monitoring wells in the vicinity of the proposed demonstration area showed that the conductivity is approximately 10^{-4} centimeters per second (cm/sec).

Based on the results of previous site investigations to evaluate measurable and significant MGP residual impacts, the area recommended for the field demonstration was in the vicinity of LB-07, along the western section of the site (shown as the target area on Figure 3-2). The selected area is impacted with both BTEX and PAH compounds. Further, the LB-07 area is located in the vicinity of the Route 9 Arterial, and is not amenable to excavation. The lithology of the target area consists of typical layers of fill material with finer grained silts underlain by till. Results of hydraulic testing performed during installation of the test wells showed that the hydraulic conductivity in the target area was approximately 8.8×10^{-5} cm/sec, similar to previous findings.

During the test well installations, it was also observed that the soils were significantly impacted by MGP residuals from approximately 10 to 16 feet bgs. Based on the observations on the soil impacts and the site hydraulics, and on the logistical issues associated with the North Water Street site, it was concluded that the Laurel Street site was the preferred location for the field demonstration.

4

BENCH-SCALE EVALUATION

MGP residuals consist of a complex mixture of compounds including PAHs, BTEX and many other large aliphatic and aromatic oils and waxes. Soil properties (e.g., sorption and desorption characteristics) and potential non-target oxidant demand (e.g., reduced minerals, naturally-occurring organic material and other contamination not quantified through TPH, PAH and BTEX analyses) can have a significant impact on oxidant performance. Bench-scale testing is recommended on representative soils from sites under consideration for treatment by ISCO. The results of the bench-scale testing are utilized in developing the field application approach and a preliminary evaluation of the ISCO cost-effectiveness. The field application approach development includes determining the mass of oxidant and number of applications required to achieve a target endpoint objective.

As discussed in Section 3, two CHGE former MGP facilities were screened to determine a site for the field demonstration of the activated persulfate ISCO technology. Preliminary bench-scale testing was conducted on soils from the North Water Street site; however, a subsequent hydraulic analysis showed that this location was not conducive to perform the field demonstration. A second CHGE facility located on Laurel Street was then selected for the field demonstration, and bench-scale tests were performed for this site. This section provides details on the performance and results of the bench-scale testing for both sites.

North Water Street Site

Soils collected from the target area at the North Water Street site were composited prior to the bench-scale testing. Preliminary bench-scale testing was designed to evaluate degradation of PAHs, and included analysis of baseline and time-series treated soil samples (at 2, 4, and 14 days).

In the preliminary testing, iron-chelate-activated persulfate was utilized. Approximately 30 grams of composite soil was added in each of the 16-ounce (oz) glass jars that were used as reactors. Subsequently, 50 milliliters (mL) solution containing 200 gram per liter (g/L) of sodium persulfate and appropriate amount of iron-chelate activator was added to the reactors. One of the reactors was setup with 30 grams of composite soil and 50 mL of the iron-chelate solution (without sodium persulfate) for the baseline soil data. The soil reactors with sodium persulfate solution were sacrificed at days 2, 4 and 14 by decanting the solution, and the treated soils were analyzed.

As shown in Figure 4-1, the results illustrate the degradation of up to 75 percent of total PAHs. The majority, if not all, of the treatment occurred within two days of the application of the activated persulfate solution.

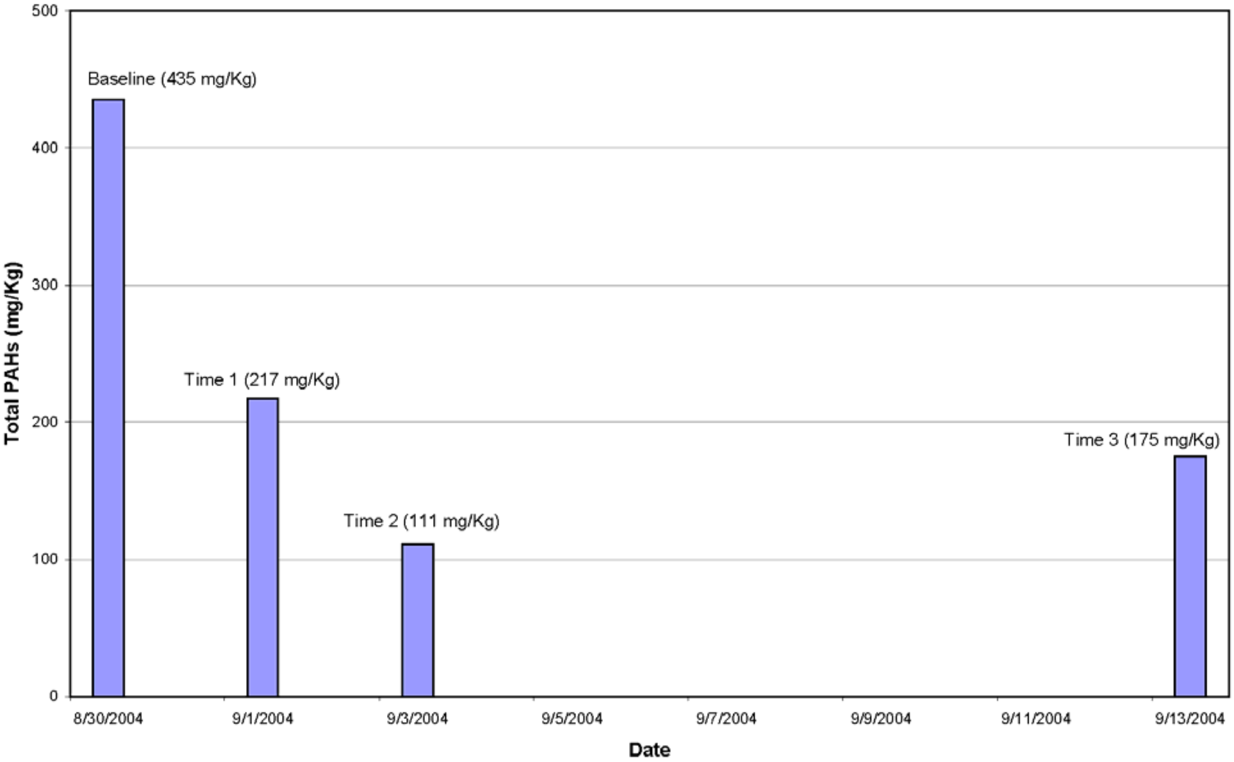

Figure 4-1
Reduction of Total PAHs in North Water Street Site Soils with Iron-Chelate-Activated Persulfate

The hydraulic analysis performed for the site suggested rapid, tidally influenced groundwater movement, which is not conducive to prolonged contact between the oxidant and the impacted soils. Therefore, the site was not considered a good candidate for the field demonstration, and no further bench-scale testing was performed on the North Water Street site soils.

Laurel Street Site

Following screening of the North Water Street site soils, a series of bench-scale tests were conducted on soils from the Laurel Street site to determine the applicability of treating the MGP-impacted soils with activated persulfate. Iron-chelate and alkaline mechanisms of persulfate activation were evaluated in this bench-scale testing.

Iron-Chelate-Activated Persulfate Evaluation

Several bench-scale tests were completed with iron-chelate-activated persulfate in the presence of soils from the Laurel Street site. The first of these tests evaluated the ability of 100 g/L, 150 g/L and 200 g/L strength sodium persulfate solutions (with proportional amounts of the activators) to degrade PAHs and TPH on soils over treatment periods of one, two, seven and 14 days. For this first test, approximately 17 mL (equivalent to approximately two pore volumes of the reactor soil volume) of reagent solution was added to 40 grams of soil composite.

The analytical data shows that the highest percent reduction in total PAHs (30 percent) and TPH (20 percent), compared to the control reactor over the 14-day treatment period, was obtained using the 200 g/L activated persulfate solution. Over the same time period, the persulfate concentration decreased an average of 38 percent in the 100 g/L, 150 g/L, and 200 g/L reactors with the majority of the sodium persulfate decomposition occurring in the first day of the reaction.

The factors that resulted in the incomplete decomposition of the persulfate were not evident and therefore were evaluated in a second series of tests. The tests were designed to evaluate a variety of factors: 1) iron to chelate ratios; 2) control of the system pH; 3) the application of excess sodium chloride; 4) use of different chelates; 5) different methods to apply chelates; and, 6) the use of excess chelate. The excess chelate and sodium chloride experiments were intended to determine if an ion from the soil, such as aluminum, or the cation exchange capacity of the soil was interfering with the activation of the sodium persulfate (i.e., tying up the iron activator).

Minimal improvements in sodium persulfate decomposition were achieved in the tests. The total decomposition of sodium persulfate remained low (approximately 50 percent) over the 6-day treatment period. Given this limitation, it was concluded that there was not sufficient confidence to consider using the iron-chelate-activated persulfate system for the field demonstration.

It was further concluded that undefined properties of the till from the Laurel Street site were interfering with the iron-chelate activation method. This conclusion was supported by numerous tests performed by XDD on MGP-impacted soils from other sites using the same reagents, which had proved to be successful at degrading the target compounds. Based on the results of the iron-chelate-activated persulfate testing, evaluation of the application of activated persulfate at the Laurel Street site using the alkaline activation method was warranted.

Alkaline-Activated Persulfate Evaluation

Alkaline-activated persulfate is based on the auto-decomposition of persulfate at elevated pH (i.e., greater than pH 10.5) (Block et al., 2004). The exact mechanism has yet to be established, but it is hypothesized that persulfate, which is stable at neutral pH, breaks apart at the oxygen (O-O) bond in the presence of an elevated pH, resulting in the formation of two sulfate radicals. Other potential mechanisms include reactions with water and hydroxide to form hydrogen peroxide and the hydroxyl radical, respectively. Despite the lack of a complete understanding of the exact mechanism, alkaline-activated persulfate has been demonstrated as a potent oxidant.

To evaluate the alkaline-activated system for the Laurel Street soils, several tests were conducted including:

- Buffering capacity of site soils;
- Auto-decomposition of alkaline-activated persulfate in the absence of site soils;
- Decomposition of alkaline-activated persulfate in the presence of site soils; and,
- Degradation of PAHs and TPH in the alkaline-activated system.

Alkaline Buffer Capacity Test

The objective of the buffering capacity testing is to determine the amount of alkaline solution (e.g., sodium hydroxide, NaOH) that is required to achieve the target pH range in a mixture of site soils and groundwater (i.e., pH greater than 10.5) for persulfate activation. The alkaline buffering capacity is determined by the presence of weak organic acids and, potentially, the mineralogy of the soil.

Results from the alkaline buffer capacity test for site soils are presented in Figure 4-2. The tests were conducted by adding one pore volume of increasing concentrations of NaOH to 40 grams of site soil. The data indicate that the site soils are buffered at a pH ranging from pH 7 to pH 10.5 and the strength of NaOH solution required per pore volume injected to raise the pH in the subsurface to above pH 10.5 is approximately 0.15 Molar.

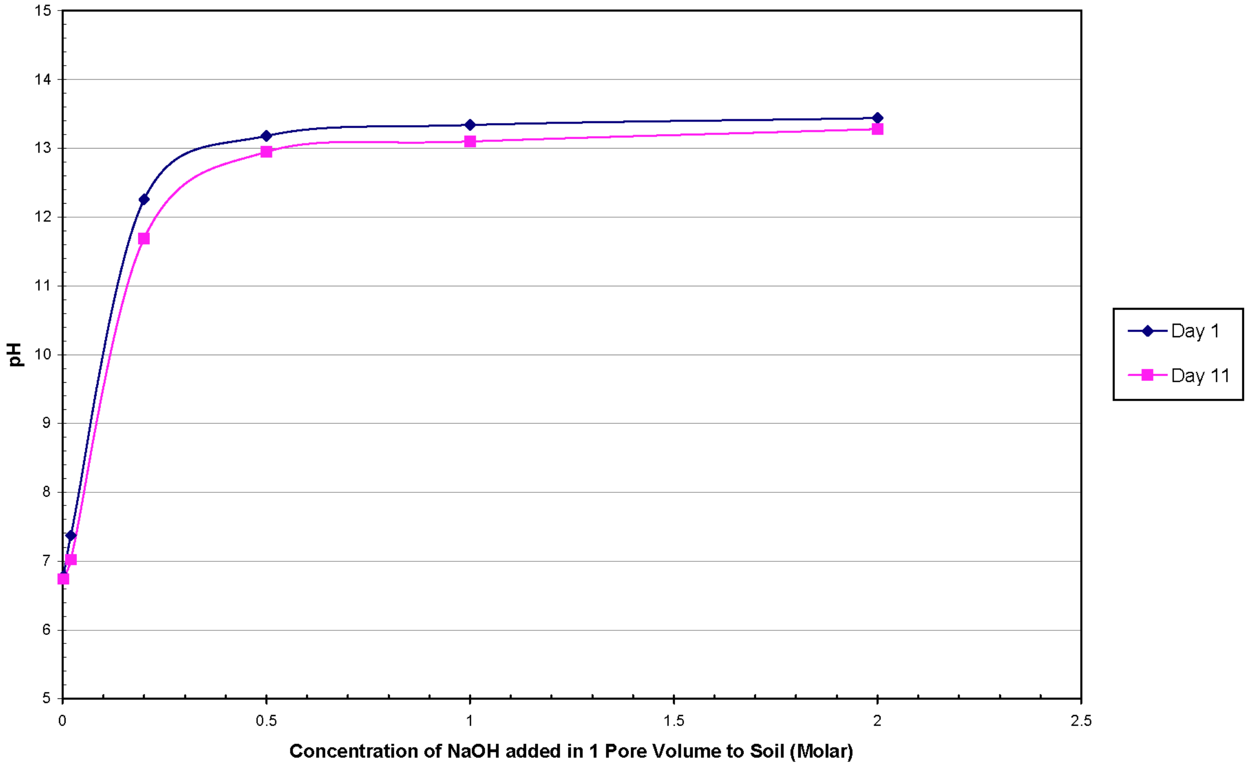

Figure 4-2
Alkaline Buffering Capacity Test on Soils, Varied NaOH, and No Persulfate

Sodium Persulfate Auto-Decomposition

The auto-decomposition of sodium persulfate in an alkaline-activated system was evaluated to assess the auto-decomposition mechanism and alkaline persulfate stability in the absence of an electron donor (i.e., oxidizable material), and the potential for aboveground batching of the sodium persulfate and sodium hydroxide solutions. This test was performed by increasing the ratio of NaOH to sodium persulfate in a 200 g/L sodium persulfate solution.

The results (Figure 4-3) show that the combined NaOH and sodium persulfate solution is relatively stable to the ratio of two moles of NaOH to one mole of persulfate (17 percent decrease in persulfate concentration over a 10-day period).

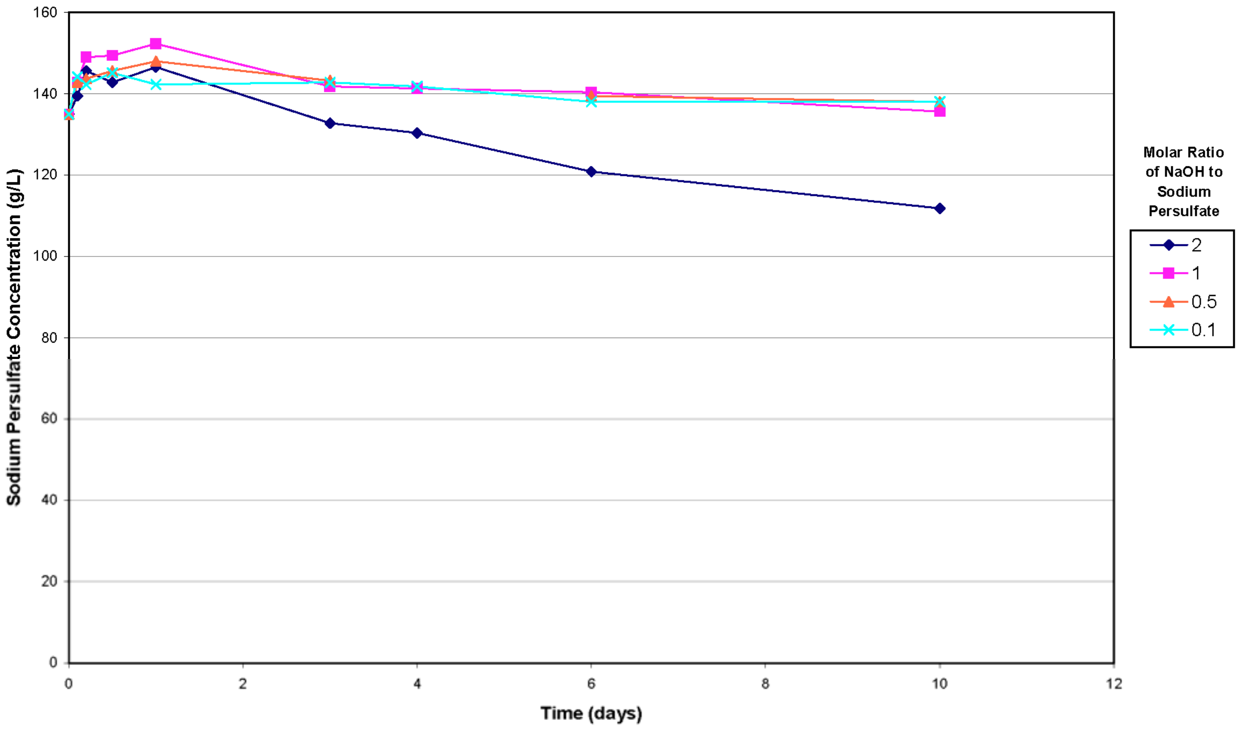

Figure 4-3
Auto-Decomposition of Persulfate: 135 g/L Persulfate, Ratio of NaOH to Persulfate Varied, No Soil

The test concluded that in the absence of oxidizable material, a mixed solution of sodium persulfate and sodium hydroxide was stable to be batched aboveground at ambient temperatures for injection within days of preparation.

Sodium Persulfate Decomposition

The objective of the sodium persulfate decomposition tests was to determine the required amount sodium hydroxide to maintain the pH above the target value of 10.5 in the presence of both the sodium persulfate and the impacted site soils. Persulfate concentration (Figure 4-4) and pH (Figure 4-5) were monitored in reactors of site soils where the ratio of NaOH to sodium persulfate was varied *(this test approach was identical to the approach described for the persulfate auto-decomposition test, except for the addition of the site soil).*

The data show that the reactor with the highest ratio of NaOH to persulfate (2:1) resulted in the highest level of persulfate decomposition (78 percent). The data also show that as the pH in each system approached or dropped below pH 10.5, the rate of persulfate decomposition decreased dramatically. The amount of persulfate that was consumed in the presence of the impacted soils was significantly greater than in the absence of the soils. The data support that the pH should be maintained above pH 10.5 to support the aggressive alkaline-activation method.

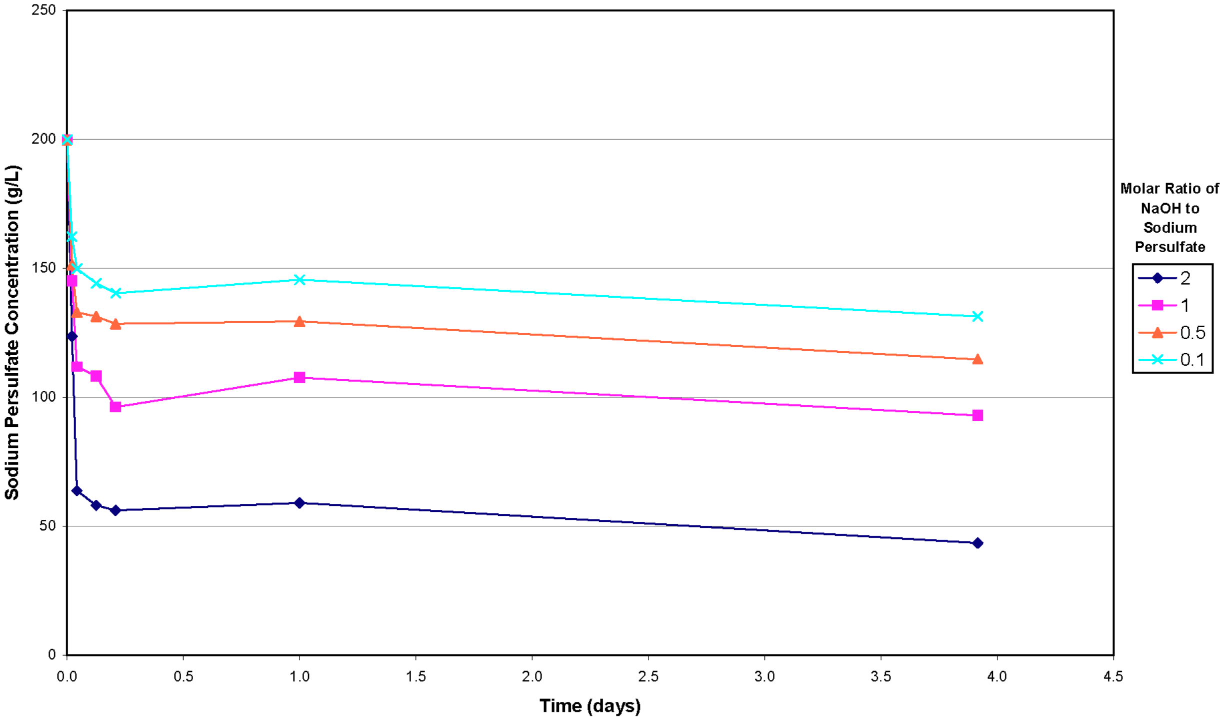

Figure 4-4
Decomposition of Persulfate on Site Soils as a Function of NaOH/Persulfate Molar Ratio

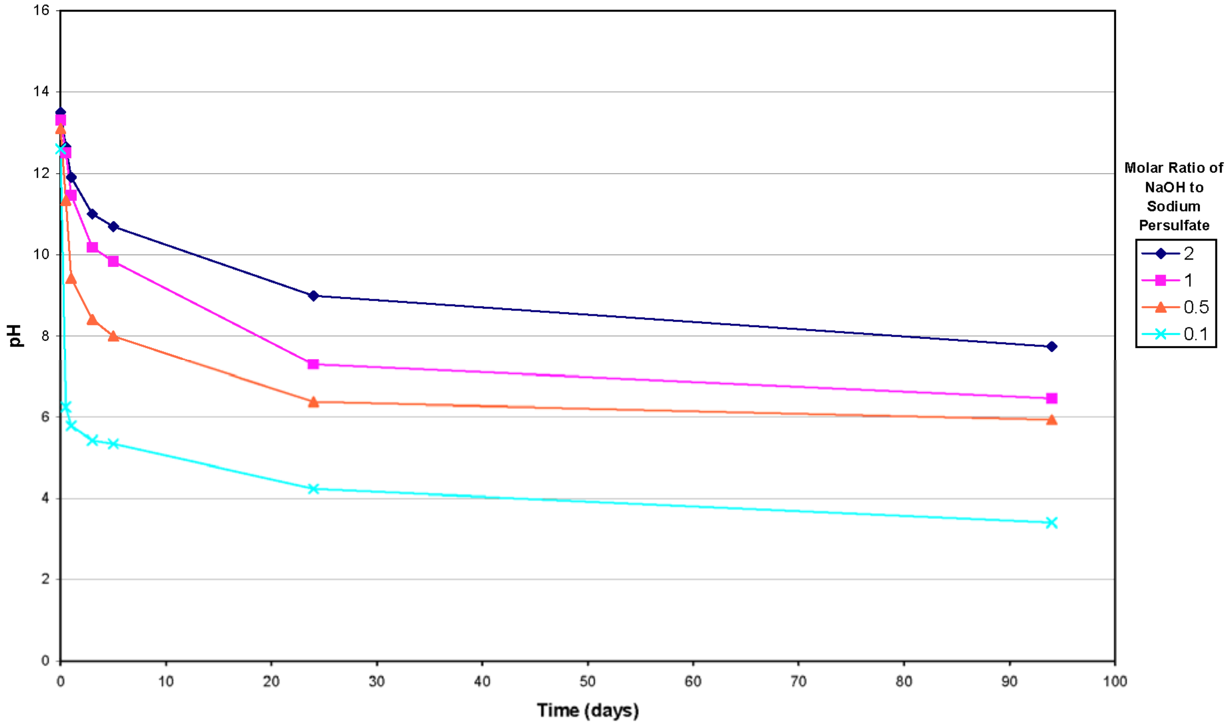

Figure 4-5
Change in pH as a Result of Persulfate Decomposition on Site Soils as a Function of NaOH/Persulfate Molar Ratio

Following the preliminary results of the persulfate decomposition testing, the rate of persulfate decomposition was evaluated using a reactor that consisted of two pore volumes of reagent solution and 40 grams of soil. The reagent solution was determined from the previous test results, and included one molar NaOH mixed with varied concentrations of sodium persulfate (50 g/L, 100 g/L and 200 g/L) with additional NaOH added periodically to maintain the reactor pH above 10.5 (the reaction between persulfate and COCs produce acids that require neutralization to maintain the target pH level in the reactor).

The data (Figure 4-6) shows that a significant portion of the persulfate was consumed within the first hour of the reaction. This is consistent with the conceptual model of persulfate reactions in a batch reactor system where the persulfate reacts with the readily available or easily desorbed compounds, and then slowly reacts with more recalcitrant or more highly sorbed compounds. The results also show that, in contrast with the iron-chelate-activated persulfate system, alkaline-activated persulfate will decompose in the presence of site soils with the limiting factor being the availability of the reactive COCs. In addition, the results showed that the 50 g/L, 100 g/L and 200 g/L sodium persulfate solutions required equivalent NaOH/sodium persulfate molar ratios of 1.0, 1.8 and 2.3, respectively, to maintain the reactor pH above pH 10.5.

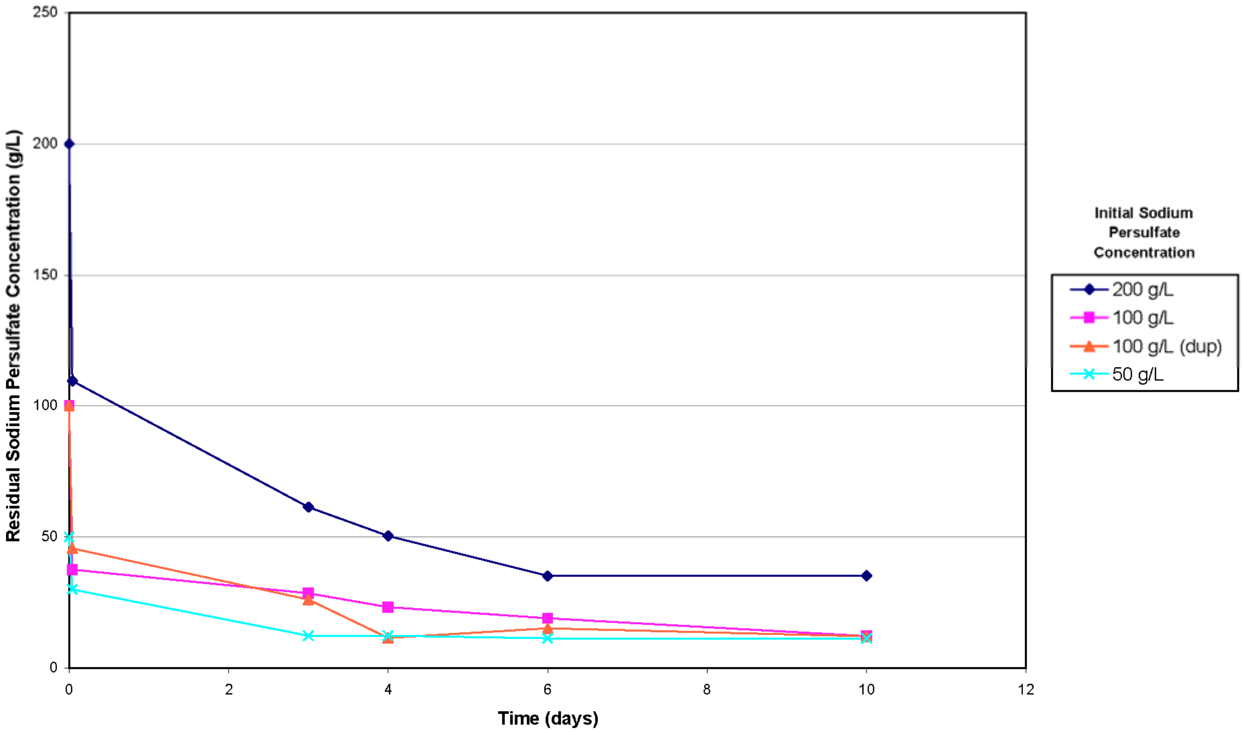

Figure 4-6
Decomposition of Persulfate in Site Soils: Initial 1 Molar NaOH, pH > 10.5 Throughout Experiment

TPH and PAH Degradation

The final bench-scale tests performed were conducted to evaluate the effectiveness of alkaline-activated persulfate for the destruction of TPH and PAHs on the site soils. Preliminary testing performed to evaluate the destruction of the TPH and PAHs utilizing the alkaline-persulfate system indicated approximately 50 percent reduction in the COC concentrations. This destruction occurred with the equivalent of one to two pore volumes of reagent solution. Persulfate reaction and TPH/PAHs destruction appear to stall after approximately 50 percent reduction.

To further evaluate this observation, chemical oxygen demand (COD) and total organic carbon (TOC) tests were conducted on the Laurel Street site soils. Results indicated that the site soils contained significant[2] non-target oxidant demand, up to 120,000 milligrams per kilogram (mg/Kg) COD, that was impeding the degradation of the COCs. As a result of this high non-target demand, a multiple application strategy was used to determine the required number of alkaline-activated persulfate application to achieve greater than 90 percent destruction of the COCs in the Laurel Street soils.

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[2] Unrelated testing performed at the University of Waterloo indicated that most natural soils have a COD in the range of up to 10,000 mg/Kg (Thomson and Xu, 2005)

Multiple applications of 200 g/L alkaline-activated persulfate solution were simulated in batch reactors. Tests were initially conducted to simulate the equivalent of two, four, and six pore volume applications by adding the appropriate amount of NaOH and sodium persulfate for two pore volumes at a time in up to three time steps of approximately three days each. Additional tests to simulate the equivalent of 10, 20, 30 and 40 pore volume applications of the alkaline-activated persulfate were performed by adding the entire equivalent mass of NaOH and persulfate at the start of the testing and allowing the reaction to proceed over a four week period.

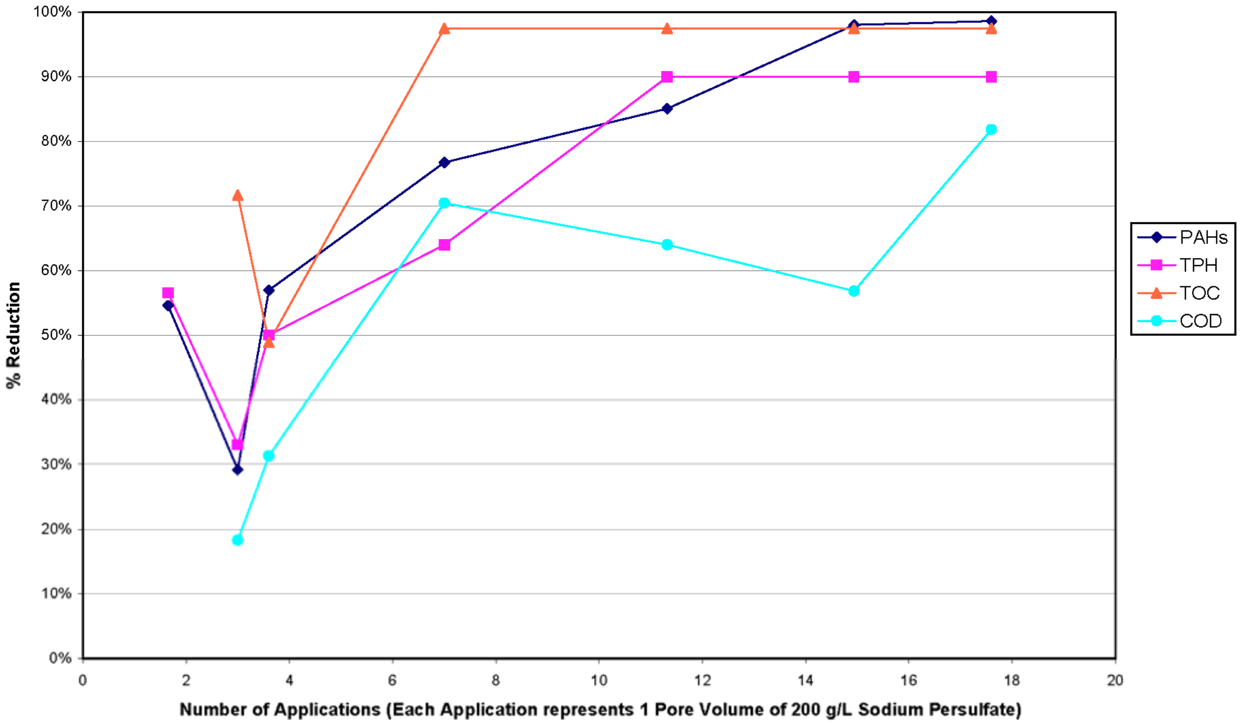


Figure 4-7
PAHs, TPH, TOC, and COD Percent Destruction Based on the Complete Decomposition of Multiple Applications of Alkaline Persulfate

The data (Figure 4-7) indicate 55 percent and 57 percent of the total PAHs and TPH were degraded with the equivalent of between one to two pore volumes of 200 g/L alkaline-activated persulfate solution. The reduction observed from the one to two pore volumes is considered to represent the degradation of the easily desorbed COCs.

The data also suggest that additional applications of 200 g/L sodium persulfate would achieve greater than 90 percent destruction of the PAHs and TPH. The significant number of applications required to achieve the 90 percent destruction are considered to represent the competition for degradation between the COD and the more highly bound portion of the COCs.

It should be noted that the predictive accuracy of the batch reactor tests in estimating the actual number of applications necessary to achieve a greater than 90 percent reduction in the COCs in the field may be difficult due to several factors including:

- the ability to scale up batch-reactor bench-scale tests to the field-scale;
- the formation of soluble and more polar products in a batch reactor and their impact on the solubility of the target compounds; and,
- that 30 percent to 56 percent of the persulfate was not consumed in these tests.

The final batch reactor tests established that a near complete oxidation of the target compounds was possible with a sufficient dose of oxidant.

Alkaline-Activated Persulfate Bench Tests: Conclusions

The bench-scale testing indicated that the alkaline activation method for persulfate was not impeded by site soil properties, unlike the iron-chelate activation method.

Furthermore, the tests demonstrated:

- Site soils required one pore volume of 0.15 Molar NaOH to achieve a pH greater than pH 10.5 in the absence of the sodium persulfate;
- The equivalent of 1.0, 1.8 and 2.3 moles of NaOH per mole of sodium persulfate was consumed for the 50 g/L, 100 g/L and 200 g/L sodium persulfate reactors, respectively, in order to maintain a pH of greater than pH 10.5 during the reaction of soils with activated persulfate;
- A solution of NaOH and sodium persulfate at ambient temperatures was stable for days; and
- Alkaline-activated persulfate was shown in bench scale that it could degrade the target COCs despite the presence of extraordinary levels of COD in the Laurel Street site soils. The high COD would require a multiple oxidant application to achieve greater than 90 percent reduction in the COCs. A cost-effective application (i.e., one to two pore volumes) was shown to conceivably achieve approximately a 50 percent reduction in COCs.

Bench-Scale Test Summary

The collective results of the bench-scale tests conducted on soils from the North Water Street and Laurel Street sites showed that iron-chelate-activated persulfate could be effective in treating soils from the North Water Street site and that alkaline-activated persulfate could be effective in treating soils from the Laurel Street site. Greater than 90 percent reductions in PAHs, TPHs and TOC concentrations were observed after persulfate utilization equivalent to approximately twelve applications.

Due to the atypically high COD measured in the Laurel Street site soils, a significant number of oxidant applications would be required to achieve a reduction in the COCs of greater than 90 percent in the field demonstration. The scope of the field demonstration did not allow for the significant number of applications. Therefore, a single application of alkaline-activated persulfate (the equivalent of one to two pore volumes of reagent solution) was selected for the field demonstration to achieve approximately 50 percent reduction in COCs (by treating readily oxidizable portion of the COCs), as observed during the bench-scale testing.

The bench tests demonstrated the importance of the soil properties on the applicability of ISCO, and the flexibility of activated persulfate to degrade MGP residuals from soil with atypically high non-target oxidant demand. Based on the bench-scale test results, alkaline-activated persulfate application was selected for field demonstration at the Laurel Street site with the expectation that approximately 50 percent reduction in TPH and PAHs would be achieved.

5

FIELD DEMONSTRATION

The field demonstration was designed to evaluate activated persulfate for the *in situ* degradation of the contaminants in site soils typically associated with MGP residuals (i.e., BTEX, PAHs and TPH). The field demonstration consisted of several steps that are discussed in this section of the report, including:

- ISCO approach;
- Field injection;
- Performance monitoring;
- Soil sampling results summary;
- Data analysis; and,
- Field application summary.

ISCO Approach

Bench-scale testing performed on soils from the Laurel Street site (as described in Section 4 of this report) identified an atypically high non-target soil oxidant demand, as represented by a COD of up to 120,000 mg/kg or 12 percent. Less than one percent COD is normal for unconsolidated materials (Thomson and Xu, 2005). Despite the high soil demand, the bench-scale test results also indicated that degradation of between 40 and 60 percent of the target compounds was possible with a single application of oxidant (i.e., one to two pore volumes). Based on an overall evaluation of the available sites, the Laurel Street site was selected for the activated persulfate demonstration.

The field demonstration approach consisted of the direct injection of alkaline-activated persulfate through a series of five injection locations to degrade the targeted MGP residuals. The ability of the activated persulfate oxidation process to decrease the mass of MGP residuals in soil and the leachability of COCs from the soils was evaluated by the following methods:

- BTEX analysis by Environmental Protection Agency (EPA) Method 8260,
- PAHs analysis by EPA Method 8270,
- TPH analysis by EPA Method 8100, and,
- Synthetic precipitation leaching procedures (SPLP) by EPA Method 1312, and then analyzing leachate for PAHs and BTEX compounds by the EPA methods listed above.

The SPLP measures the partitioning of target compounds from treated soils into simulated groundwater, and was used to measure the leaching characteristics of the site soils before and after the single application of activated persulfate. The SPLP analysis is an important ISCO performance evaluation tool, as groundwater is a primary exposure pathway for contamination to environmental receptors. Based on the bench-scale testing results, the expectation for the single application of activated persulfate was to achieve approximately 50 percent reduction in TPH and PAHs in the soil.

Five injection points (IP-1 through IP-5) and four monitoring points (MP-1 through MP-4) were installed in and around the target treatment area (Figure 5-1). In addition, a previously installed monitoring well, MW-5, was utilized in the monitoring point network. All the installed wells were designed with a sand pack interval from 11 ft bgs to 16 ft bgs (the target vertical treatment volume). In low conductivity soils, like those encountered at the site, the treatment interval will typically correspond to the sand pack interval.

The injection points were situated to provide maximum coverage of the target area, assuming a limited radius of influence of three feet from each injection point due to the relatively low soil hydraulic conductivity determined from the tests conducted on the installed wells and the time and budget limitations for the project. The monitoring points were situated with MP-1 and MP-2 at the edges of the target treatment area, MP-3 between two injection points (IP-3 and IP-4), and MP-4 and MW-5 located downgradient of the target area.

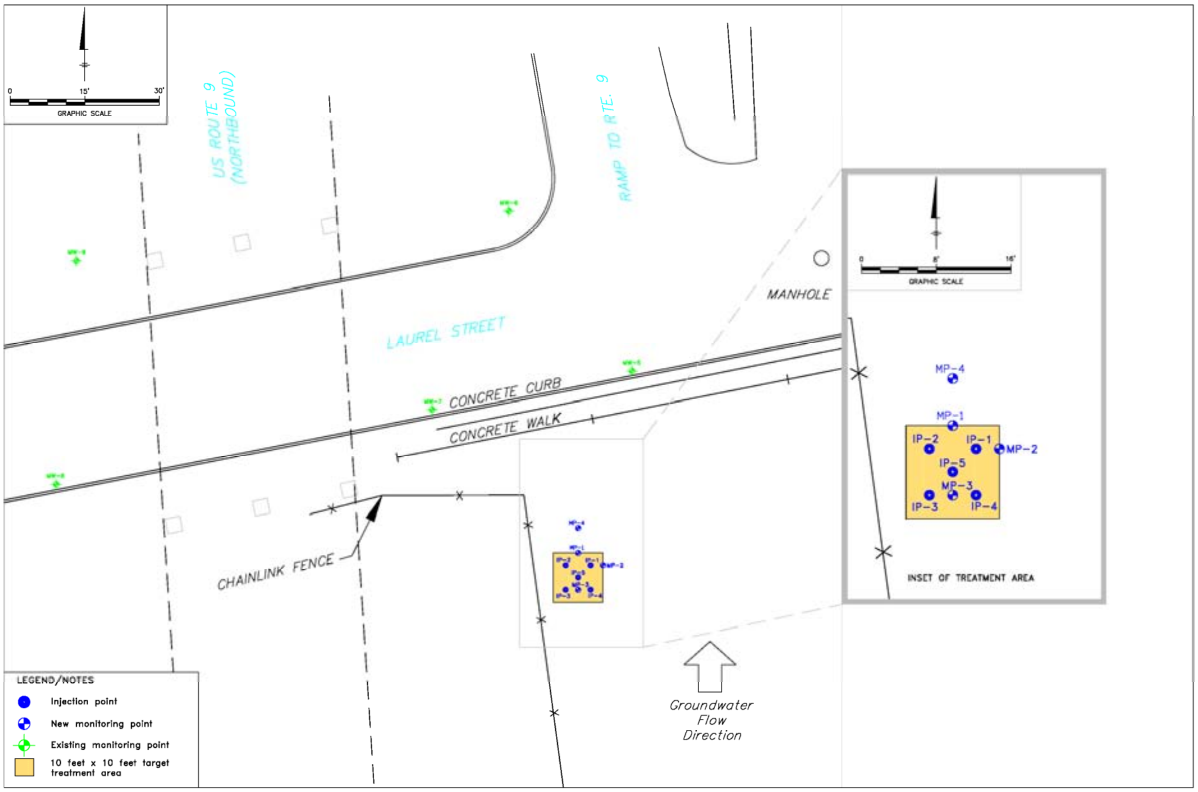


Figure 5-1
Site Layout and Target Treatment Area

Field Injection

XDD field crews, with support from BBL-Arcadis, were onsite from April 24, 2006 to April 28, 2006 to conduct the field demonstration. Shown in Figure 5.2, XDD's Portable Oxidant Delivery (POD) system was used to batch and inject the reagent solution into the target area. Sodium hydroxide, also known as caustic soda, was used to activate the sodium persulfate *in situ* by raising the pH to above pH 10.5 in the target soil volume. As presented in Table 5-1, approximately 6,270 pounds of powdered sodium persulfate was dissolved into a NaOH solution and injected simultaneously into IP-1 through IP-5 at concentrations of approximately 250 g/L of sodium persulfate and 140 g/L of sodium hydroxide.

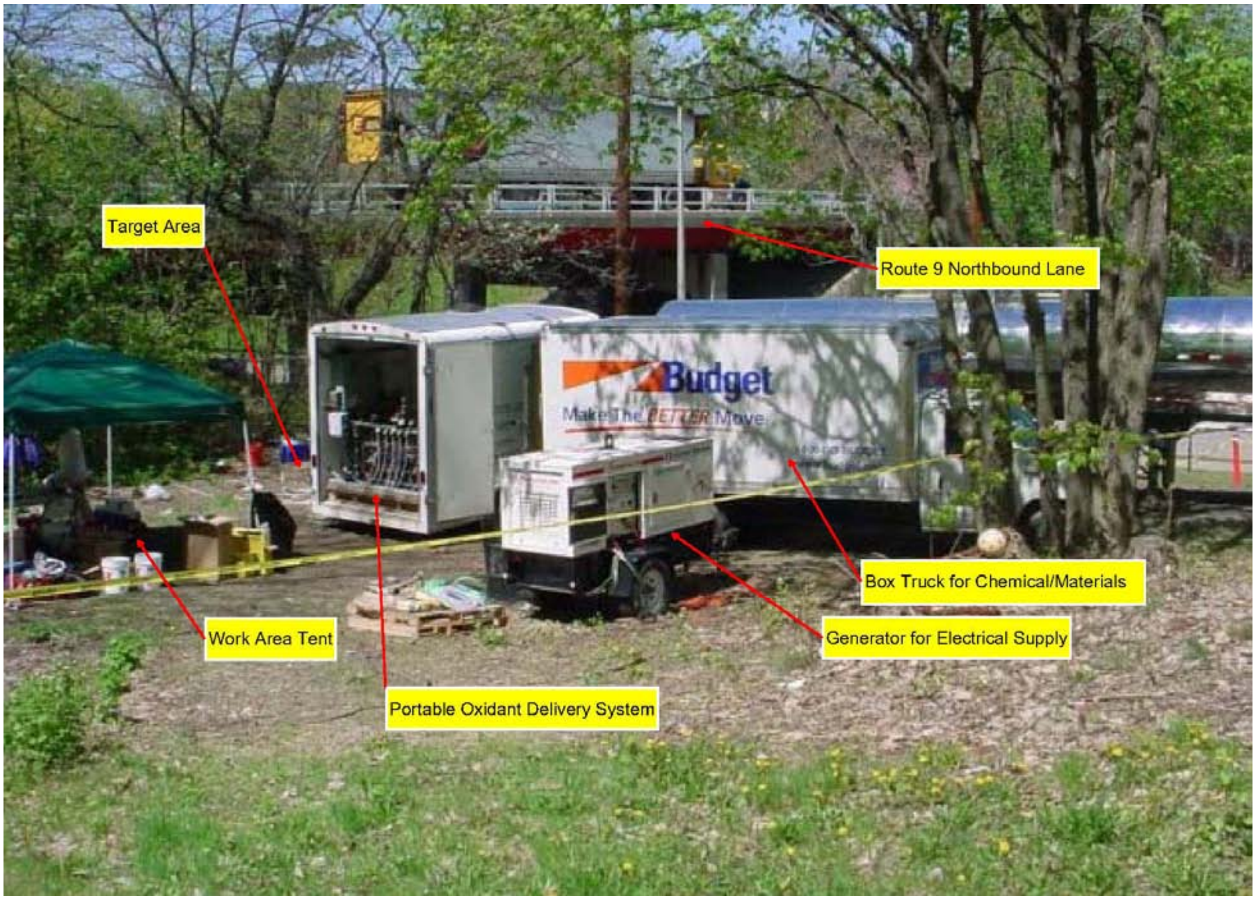
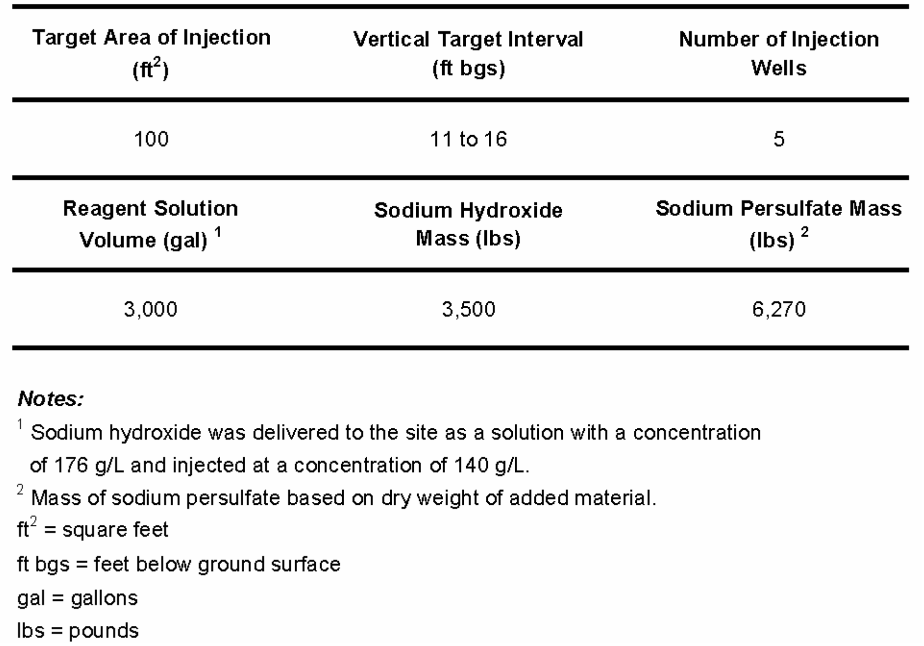


Figure 5-2
Field Demonstration Set-Up

A total of twelve 250-gallon batches of sodium persulfate and NaOH solution were mixed and injected over the course of the application. Each batch consisted of 520 pounds of granular form sodium persulfate. The total of 3,000 gallons of injection was equivalent to approximately 2.7 pore volumes of the target area.

If an ISCO application is not engineered or applied appropriately, the injected solution from subsurface could travel along the injection or monitoring boreholes to the ground surface (commonly known as short-circuiting). The appearance of the strong oxidant solution on ground surface is a health and safety issue. During the ISCO application at the Laurel Street site, the injected solution remained in the ground and no short-circuiting to the ground surface was observed.

Table 5-1
Summary of Injection



Target Area of Injection (ft^2)	Vertical Target Interval (ft bgs)	Number of Injection Wells
100	11 to 16	5
Reagent Solution Volume (gal) [1]	**Sodium Hydroxide Mass (lbs)**	**Sodium Persulfate Mass (lbs) [2]**
3,000	3,500	6,270

Notes:

[1] Sodium hydroxide was delivered to the site as a solution with a concentration of 176 g/L and injected at a concentration of 140 g/L.

[2] Mass of sodium persulfate based on dry weight of added material.

ft^2 = square feet

ft bgs = feet below ground surface

gal = gallons

lbs = pounds

Performance Monitoring

As presented in the following subsections, the performance of the field demonstration was monitored via several different methods including:

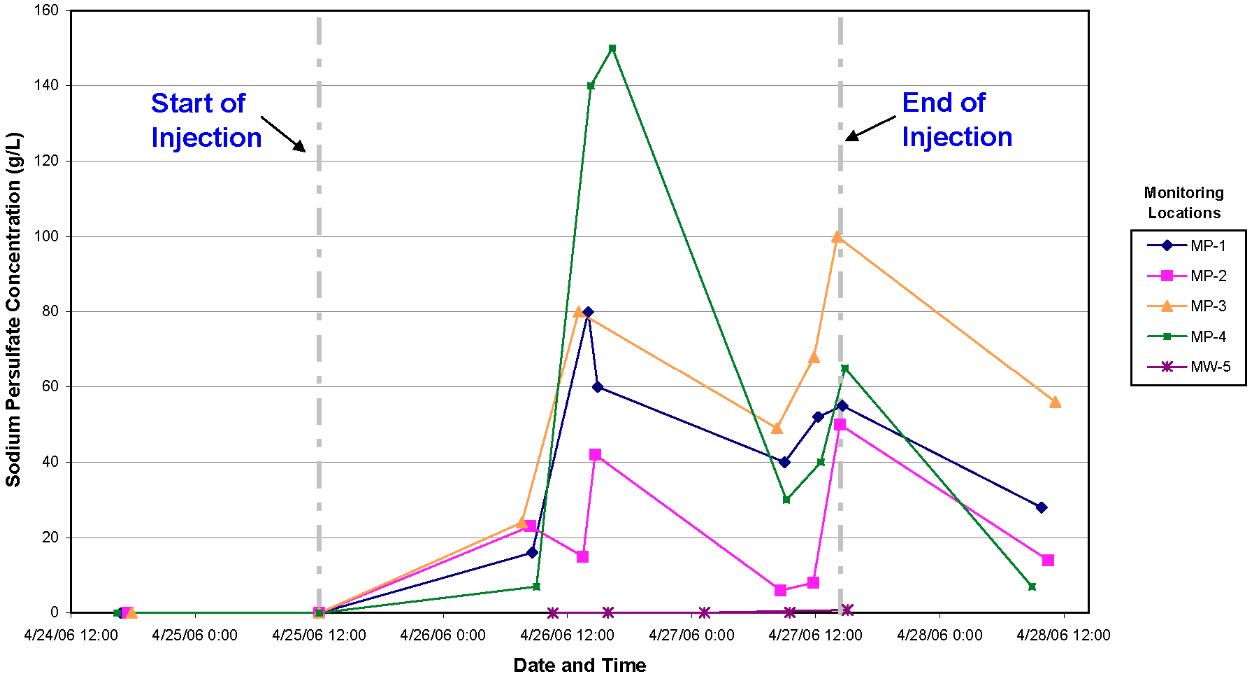
- Field parameters;
- Visual observations;
- TarGOST® analysis;
- Groundwater sampling; and
- Soil sampling.

Field Parameter Monitoring

During the injection event, process monitoring included measuring field parameter data [i.e., pH, oxidation-reduction potential (ORP), conductivity, dissolved oxygen, temperature, groundwater elevation, and sodium persulfate concentration] collected from MP-1 through MP-4 and MW-5.

The data show that the pH in the target area stayed above pH 12 for the duration of the injection event, facilitating activation of the sodium persulfate. In addition, the conductivity in the target area increased by two to three orders of magnitude, and the temperature increased between 8 degrees Celsius (°C) and 11°C from the baseline, peaking at 19.5°C at MP-3. It is hypothesized that this temperature increase may be due to both the mildly exothermic reactions and as a result of the ambient heat transferred to the aquifer through the injected reagent solution.

Residual persulfate concentrations in groundwater (Figure 5-3) in the target area ranged from 6 to 150 g/L during the injection. Lower concentrations were observed in the early morning readings on days following an injection, indicating active reactions with the persulfate. ORP values increased to over 200 milli-volts (mV) during injection, indicating oxidizing conditions. The collective data indicate that persulfate was well distributed in the subsurface within the target soil volume and that the necessary conditions for alkaline-activated persulfate were obtained.



Note:
Post-application monitoring for residual persulfate was also conducted in May 2006. Residual persulfate concentration at all locations with the exception of MW-5 (0.2 g/L) was below the detection limit.

Figure 5-3
Sodium Persulfate Concentration in Groundwater

The data also clearly show significant impacts of the injection outside of the target area. Residual persulfate concentrations as high as 150 g/L, and increases in ORP to 429 mV and pH greater than 12, respectively, were observed at MP-4 (approximately five feet downgradient of the target area) during the application. Similarly, residual persulfate concentrations of 0.8 g/L persulfate, and increases in ORP to 242 mV and pH 12, respectively, were measured at MW-5, approximately 50 feet downgradient of the target area.

NAPL Observations

There was no measurable NAPL accumulation in the monitoring points over the duration of the field demonstration. A sheen of light NAPL (LNAPL) was observed in immeasurable quantities at MP-1 through MP-4 on objects such as sampling tubing. However, the LNAPL was observed prior to, during, and after the injection activities, indicating that the presence of LNAPL was not as a result of the injection activities. During and immediately following the injections, increases in groundwater elevations, ranging from 0.8 to 4.3 feet, were observed at all of the monitoring points.

Soil Sampling

The primary method used to evaluate the performance of the activated persulfate application on the MGP residuals was soil sampling. Soil samples were collected prior to (baseline) and after (post-application) the activated persulfate application. The soil samples for both the baseline and post-application samples were collected in close proximity to MP-1, MP-3, MP-4, IP-1, IP-2, and IP-3 (Figure 5-4) to create sample pairs for comparison. Additional baseline soil samples were collected at XDD-1, XDD-2, and additional post-application soil samples were collected from near MP-2. Samples were collected from two vertical intervals, within the 11 to 16 feet bgs target vertical treatment interval, at each location. Shallow samples were typically collected from 12 to 14 feet bgs and deep samples were collected from 14 to 16 feet bgs. Soil samples were collected using both grab and composite sampling techniques (using the standard operating procedures outlined in the field demonstration work plan) and shipped to Premier Laboratory of Dayville, Connecticut for analysis of the following parameters: PAHs, BTEX, TPH, PAH SPLP, BTEX SPLP, TOC, and COD.

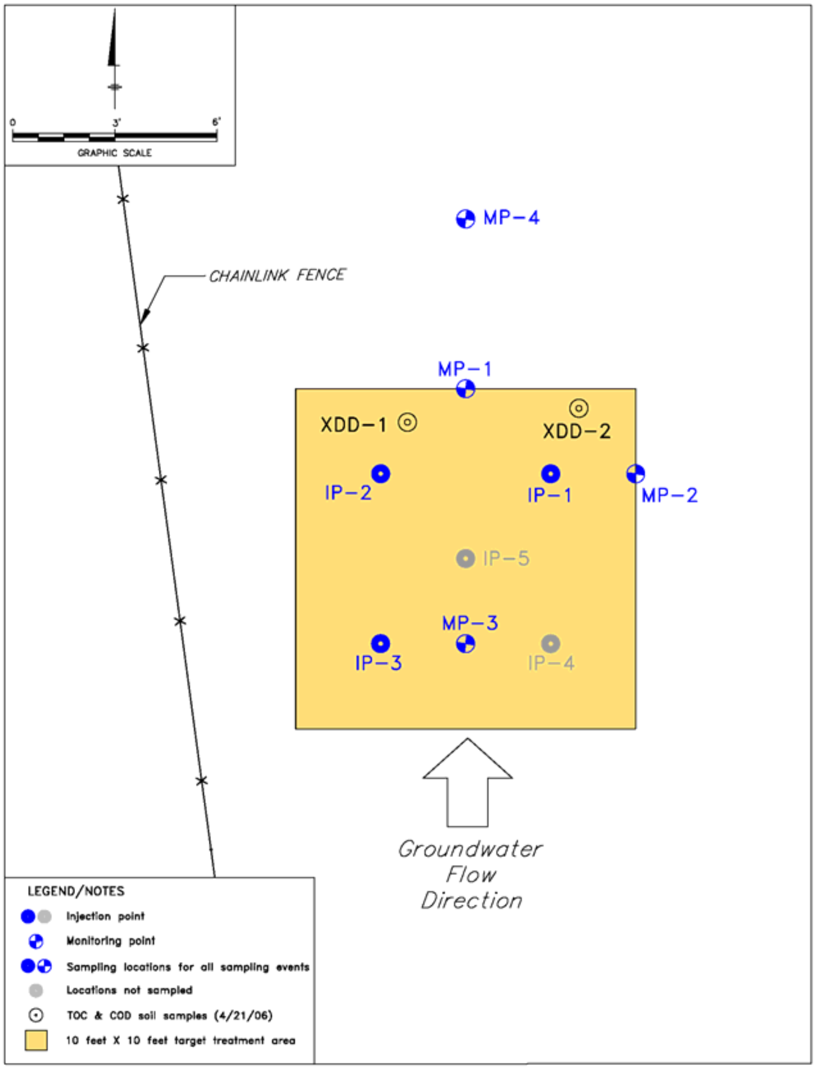
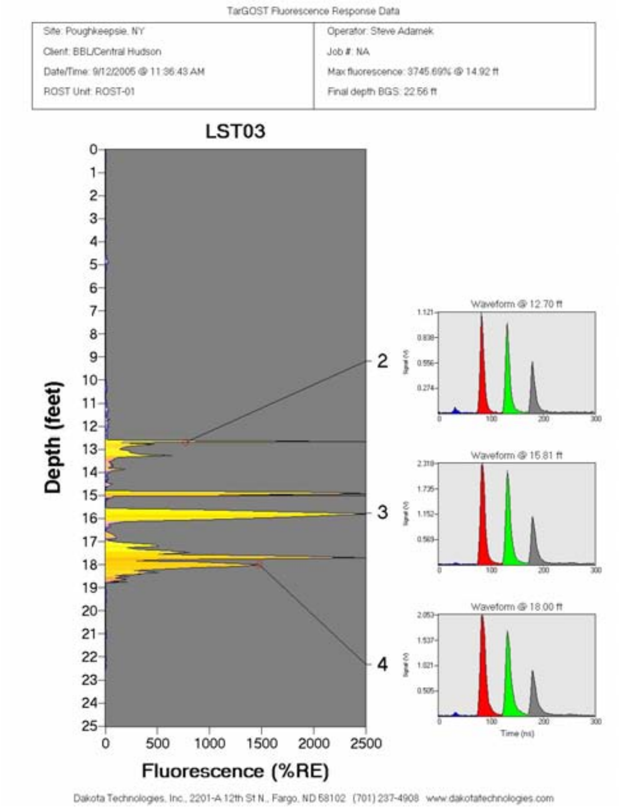


Figure 5-4
Soil Sampling Locations

TarGOST® Sampling

As a part of the baseline sampling TarGOST® profiling was conducted at several locations in and around the target area to refine the understanding of the architecture of the NAPL distribution. TarGOST® logs from two of the locations within the target area are presented as Figures 5-5 and 5-6. The TarGOST® profiling logs show that high level of contamination is distributed in the vertical interval ranging from 10 to 19 ft bgs. A post-application TarGOST® profiling was not conducted.

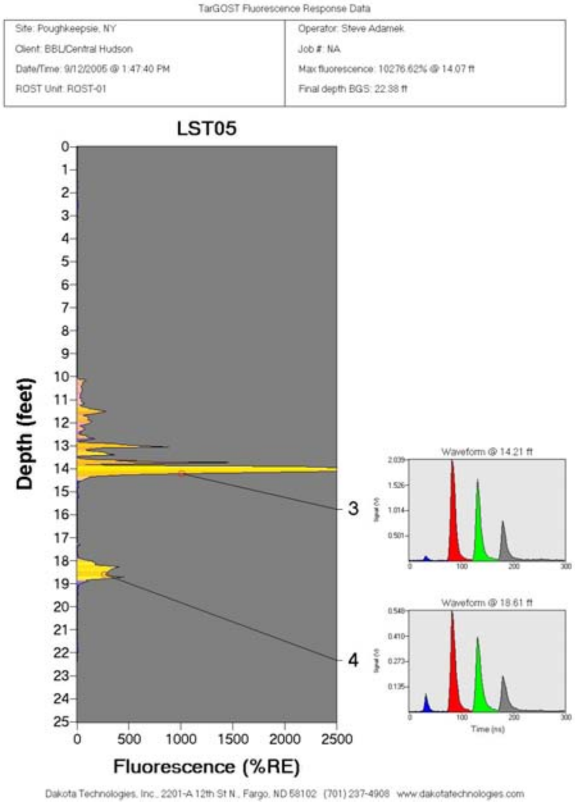


TarGOST Fluorescence Response Data

Site: Poughkeepsie, NY	Operator: Steve Adamek
Client: BBL/Central Hudson	Job #: NA
Date/Time: 9/12/2005 @ 11:36:43 AM	Max fluorescence: 3745.69% @ 14.92 ft
ROST Unit: ROST-01	Final depth BGS: 22.56 ft

Dakota Technologies, Inc., 2201-A 12th St N., Fargo, ND 58102 (701) 237-4908 www.dakotatechnologies.com

Figure 5-5
TarGOST Profiling Log: Location LST03



TarGOST Fluorescence Response Data

Site: Poughkeepsie, NY
Client: BBL/Central Hudson
Date/Time: 9/12/2005 @ 1:47:40 PM
ROST Unit: ROST-01
Operator: Steve Adamek
Job #: NA
Max fluorescence: 10276.62% @ 14.07 ft
Final depth BGS: 22.38 ft

Dakota Technologies, Inc., 2201-A 12th St N., Fargo, ND 58102 (701) 237-4908 www.dakotatechnologies.com

Figure 5-6
TarGOST Profiling Log: Location LST05

Groundwater Sampling

The results of the groundwater analyses were intended to show any impacts on the leachability of the target compounds into groundwater over a larger soil volume than represented by soil SPLP analyses. Two sets of groundwater samples were collected from the four monitoring points (MP-1 through MP-4), and analyzed for BTEX, PAHs and TPH: a baseline data set prior to start of oxidant injection (April 24, 2006) and a post-application data set collected at the conclusion of the field injection work (April 28, 2006). The objective of post-application groundwater data collection was to evaluate the change in leachable contaminant concentrations from the treated soils due to the oxidant application, as measured from influx of clean, upgradient groundwater into the treatment area. However, groundwater field parameter data collected during two subsequent post-application monitoring events (May 24, 2006 and June 13, 2006) showed elevated pH, indicating that the spent oxidant solution was still within the target soil volume, and therefore, post-application groundwater data were not collected. Due to unavailability of the post-application groundwater data for comparison and evaluation, the groundwater data were not presented in this report.

Soil Sampling Data Summary

The total BTEX, total PAH and TPH concentration data from the composite and grab soil samples and the composite soil sample for SPLP analysis are summarized in Tables 5-2 and Figures 5-7, 5-8 and 5-9. Tables 5-3 through 5-8 present the soil concentration data of the individual compounds for BTEX and PAHs.

The baseline and post-application soil samples were collected from two intervals at five locations (four locations within and one location outside the target area) to create sample pairs for data comparison and evaluation against the expectations for the field demonstration. Further, the sampling methods were assessed by analyses of total concentration of PAHs, BTEX and TPH from samples collected using both grab and interval composite sampling techniques. The leaching characteristics of the soils, evaluated by SPLP analyses, were only determined using composite soil samples.

Composite Soil Sample Results

Composite samples are considered representative for the evaluation of remedial measures for soils with highly variable contaminant impacts, as is the case at most former MGP sites. As specified above, composite soil samples were collected at two vertical intervals at five locations (IP-1, IP-2, IP-3, MP-1, and MP-3) within the target area and from a single interval at one location (MP-4) outside the target area. The results of the composite soils analyses are presented in Tables 5-3 and 5-4 and Figure 5-5. The following is a brief comparison of the baseline and post-application results for the composite soil samples:

- Total PAHs: Of the 11 sample pair sets, nine showed a net decrease in PAH soil concentration, and the other two showed net increases. The overall average decrease in total PAH concentrations was approximately 55 percent.
- Total BTEX: Of the nine sample sets with both baseline and post-application BTEX data, four indicated a decrease in BTEX concentration and the remaining five sample sets showed increases in BTEX concentration. The overall change in average of total BTEX concentrations was insignificant.
- TPH: Similar to the PAHs, the same nine of 11 sample sets showed decreases in TPH concentration and the remaining two sets showed an increase. The overall average decrease in TPH concentrations was approximately 68 percent.

Table 5-2
Baseline and Post-Application Results Summary for Soil Data

Boring	Depth Below Grade (feet)	COMPOSITE SAMPLES (mg/Kg)										COMPOSITE SPLP (mg/L)				GRAB SAMPLES (mg/Kg)			
		Total PAHs		Total BTEX		TPH		TOC		COD		Total PAHs		Total BTEX		Total PAHs		Total BTEX	
		Baseline	Post	Baseline	Post	Baseline	Post	Baseline	Post	Baseline	Post	Baseline	Post	Baseline	Post	Baseline	Post	Baseline	Post
IP-1	12-14	743	233	387	249	4,300	550	-	-	-	-	6.0	3.1	6.6	6.0	1,198	868	366	364
	14-16	916	368	273	437	4,500	820	-	-	-	-	-	3.1	-	7.7	-	-	-	-
IP-2	10-12	2,542	978	300	303	6,100	2,100	-	11,000	-	89,000	-	2.8	6.6	2.6	-	-	-	-
	12-14	3,379	755	404	299	6,400	1,800	-	9,300	-	82,000	4.9	3.1	-	5.1	3,239	705	747	207
IP-3	12-14	846	560	234	17	2,800	740	-	-	-	-	-	-	-	-	-	-	-	-
	14-16	520	1,070	90	330	2,700	3,100	-	-	-	-	-	-	-	-	-	-	-	-
MP-1	12-14	1,822	503	-	204	4,600	1,300	-	-	-	-	8.2	2.1	6.1	5.2	1,817	685	276	273
	14-16	645	405	233	189	1,200	710	-	-	-	-	-	2.0	-	5.3	-	-	-	-
MP-2	12-14	-	746	-	320	-	1,500	-	7,800	-	90,000	-	3.0	-	6.3	-	966	-	466
	14-16	-	486	-	184	-	900	-	9,600	-	46,000	-	-	-	-	-	-	-	-
MP-3	12-14	682	292	84	149	2,700	1,200	-	-	-	-	5.7	1.1	2.0	2.0	507	764	92	140
	14-16	524	1,137	90	204	2,000	2,300	-	-	-	-	-	2.9	-	5.6	-	-	-	-
MP-4	13.5-14.5	2,462	444	-	399	12,000	1,400	-	-	-	-	-	-	-	-	-	-	-	-
XDD-1	12-14	-	-	-	-	-	-	1,100	-	25,000	-	-	-	-	-	-	-	-	-
	14-16	-	-	-	-	-	-	12,000	-	42,000	-	-	-	-	-	-	-	-	-
XDD-2	12-14	-	-	-	-	-	-	20,000	-	44,000	-	-	-	-	-	-	-	-	-
	14-16	-	-	-	-	-	-	10,000	-	27,000	-	-	-	-	-	-	-	-	-
Average (paired data*)		1,371	613	233	242	4,482	1,456					6.2	2.3	5.3	3.9	1,690	756	370	246
% Reduction*			**55%**		**-4%**		**68%**						**62%**		**27%**		**55%**		**34%**

Notes:

mg/Kg = milligrams per kilogram

SPLP = Synthetic Precipitation Leachate Procedure

mg/L = milligrams per liter

PAHs = Polycyclic Aromatic Hydrocarbons

Post = post-application

BTEX = Benzene, Toluene, Ethylbenzene and Xylene

TPH = Total Petroleum Hydrocarbons

TOC = Total Organic Carbon

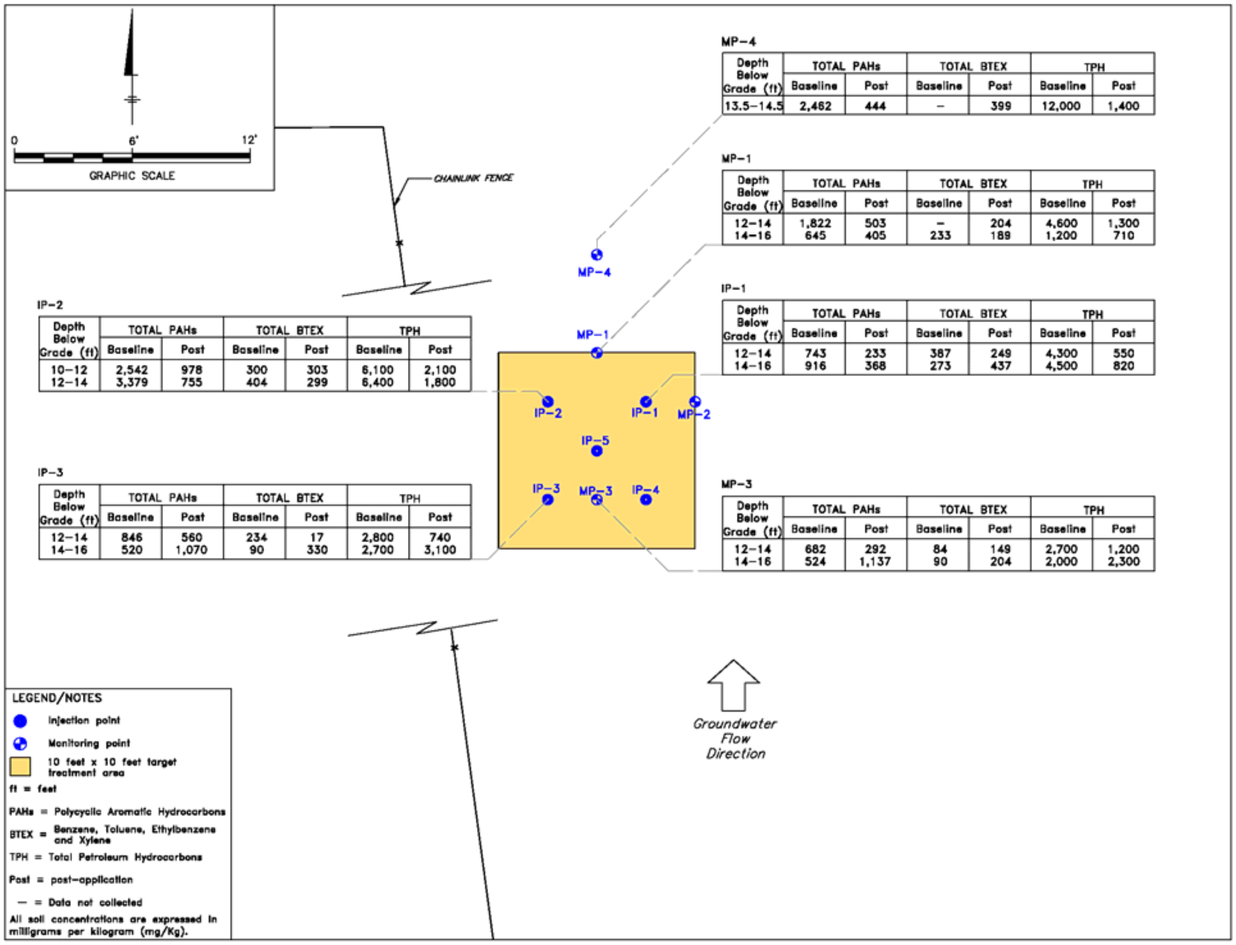
COD = Chemical Oxygen Demand

- = data not collected

🟨 post-application contaminant concentration < baseline contaminant concentration

🟦 post-application contaminant concentration > baseline contaminant concentration

* = "Average" and "% Reduction" are calculated using **paired data** only (data from intervals sampled during both baseline and post-application sampling events).



MP-4

Depth Below Grade (ft)	TOTAL PAHs		TOTAL BTEX		TPH	
	Baseline	Post	Baseline	Post	Baseline	Post
13.5–14.5	2,462	444	–	399	12,000	1,400

MP-1

Depth Below Grade (ft)	TOTAL PAHs		TOTAL BTEX		TPH	
	Baseline	Post	Baseline	Post	Baseline	Post
12–14	1,822	503	–	204	4,600	1,300
14–16	645	405	233	189	1,200	710

IP-1

Depth Below Grade (ft)	TOTAL PAHs		TOTAL BTEX		TPH	
	Baseline	Post	Baseline	Post	Baseline	Post
12–14	743	233	387	249	4,300	550
14–16	916	368	273	437	4,500	820

IP-2

Depth Below Grade (ft)	TOTAL PAHs		TOTAL BTEX		TPH	
	Baseline	Post	Baseline	Post	Baseline	Post
10–12	2,542	978	300	303	6,100	2,100
12–14	3,379	755	404	299	6,400	1,800

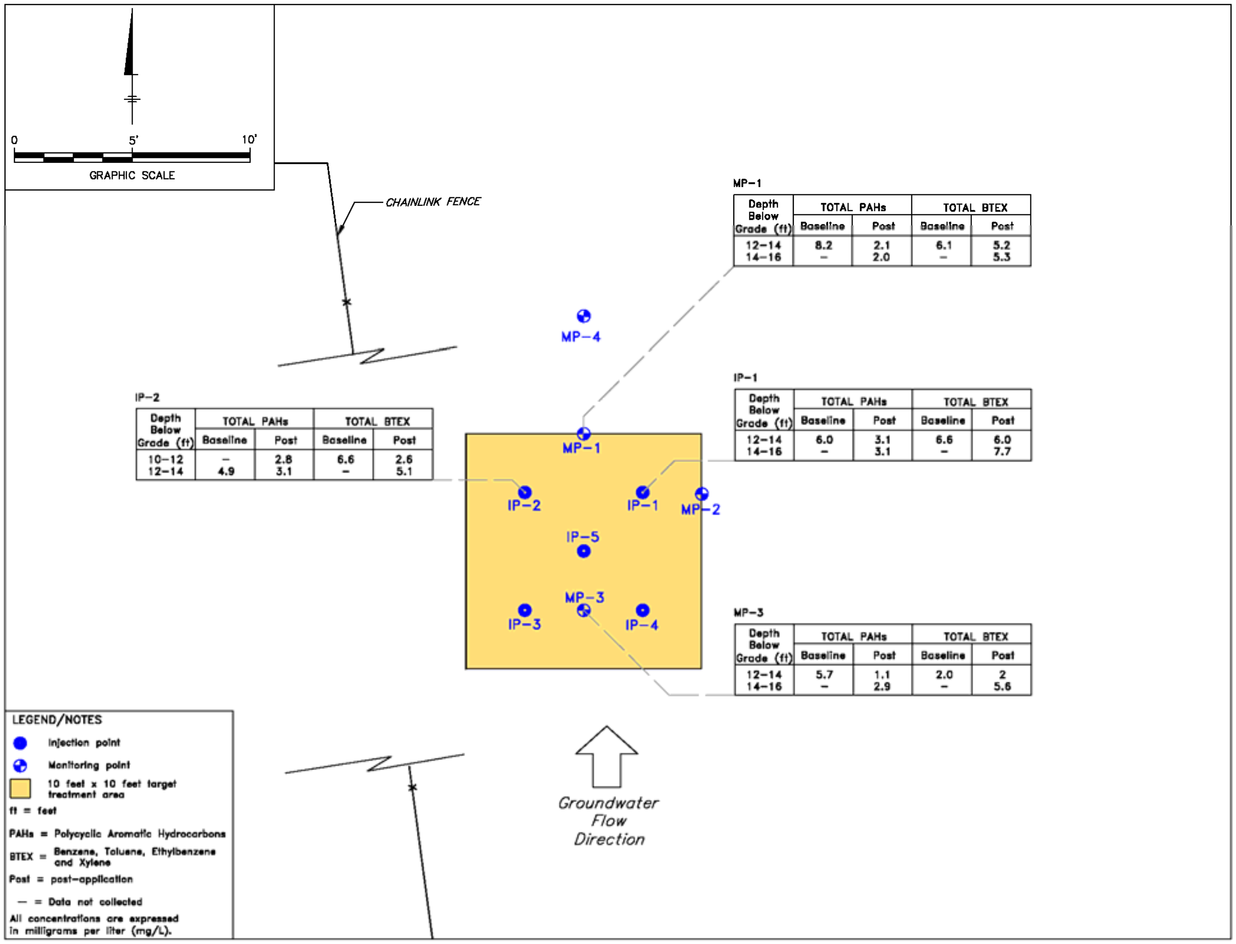
IP-3

Depth Below Grade (ft)	TOTAL PAHs		TOTAL BTEX		TPH	
	Baseline	Post	Baseline	Post	Baseline	Post
12–14	846	560	234	17	2,800	740
14–16	520	1,070	90	330	2,700	3,100

MP-3

Depth Below Grade (ft)	TOTAL PAHs		TOTAL BTEX		TPH	
	Baseline	Post	Baseline	Post	Baseline	Post
12–14	682	292	84	149	2,700	1,200
14–16	524	1,137	90	204	2,000	2,300

Figure 5-7
Baseline and Post-Application Composite Soil Sample Results for Total PAH, BTEX, and TPH Compounds



MP-1

Depth Below Grade (ft)	TOTAL PAHs		TOTAL BTEX	
	Baseline	Post	Baseline	Post
12-14	8.2	2.1	6.1	5.2
14-16	–	2.0	–	5.3

IP-1

Depth Below Grade (ft)	TOTAL PAHs		TOTAL BTEX	
	Baseline	Post	Baseline	Post
12-14	6.0	3.1	6.6	6.0
14-16	–	3.1	–	7.7

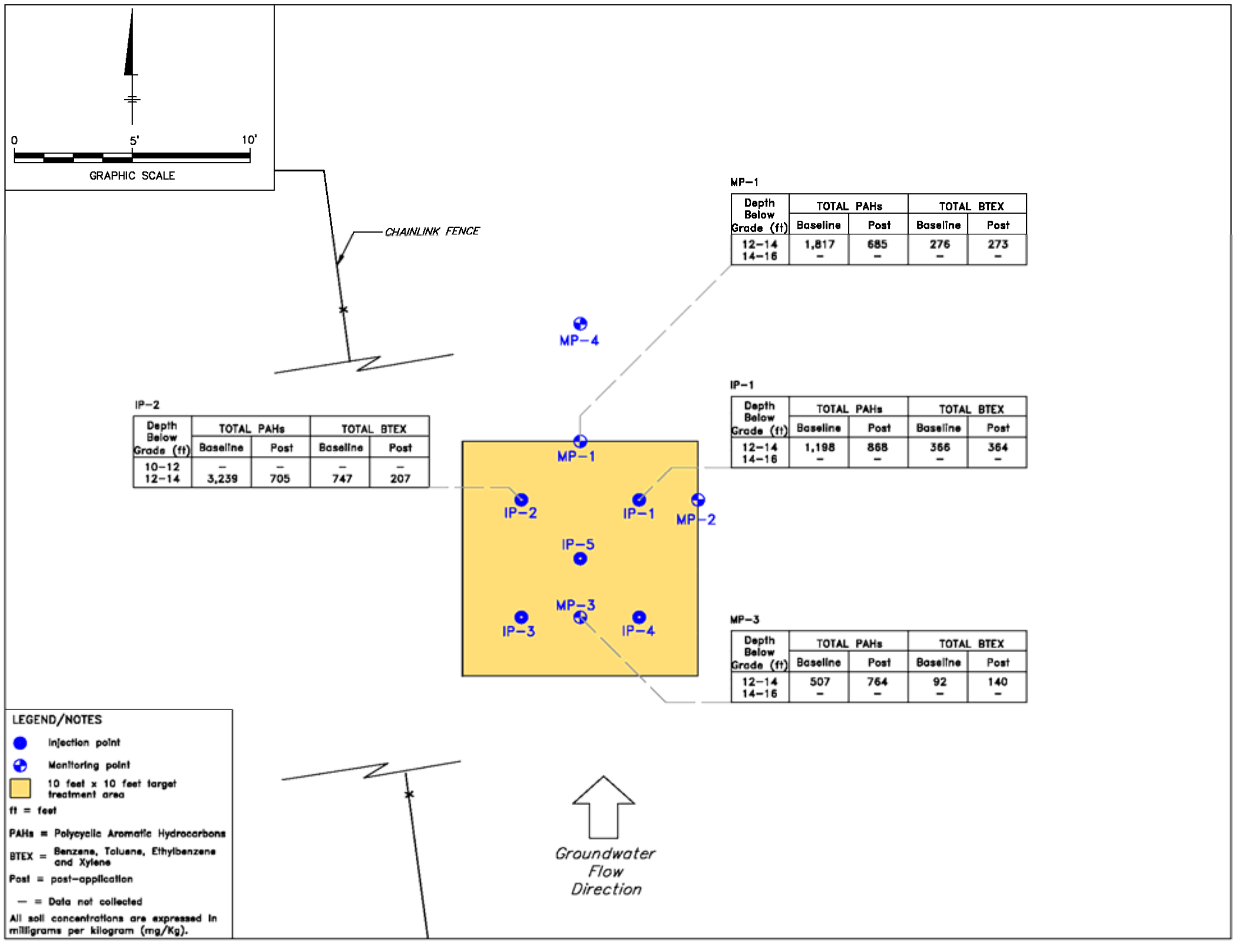
IP-2

Depth Below Grade (ft)	TOTAL PAHs		TOTAL BTEX	
	Baseline	Post	Baseline	Post
10-12	–	2.8	6.6	2.6
12-14	4.9	3.1	–	5.1

MP-3

Depth Below Grade (ft)	TOTAL PAHs		TOTAL BTEX	
	Baseline	Post	Baseline	Post
12-14	5.7	1.1	2.0	2
14-16	–	2.9	–	5.6

Figure 5-8
Baseline and Post-Application Grab Soil Sample Results for Total PAH and BTEX Compounds



MP-1

Depth Below Grade (ft)	TOTAL PAHs		TOTAL BTEX	
	Baseline	Post	Baseline	Post
12-14	1,817	685	276	273
14-16	—	—	—	—

IP-2

Depth Below Grade (ft)	TOTAL PAHs		TOTAL BTEX	
	Baseline	Post	Baseline	Post
10-12	—	—	—	—
12-14	3,239	705	747	207

IP-1

Depth Below Grade (ft)	TOTAL PAHs		TOTAL BTEX	
	Baseline	Post	Baseline	Post
12-14	1,198	868	366	364
14-16	—	—	—	—

MP-3

Depth Below Grade (ft)	TOTAL PAHs		TOTAL BTEX	
	Baseline	Post	Baseline	Post
12-14	507	764	92	140
14-16	—	—	—	—

Figure 5-9
Baseline and Post-Application SPLP Results for Total PAH and BTEX Compounds

Table 5-3
PAH Results for Composite Soil Samples

Boring	Sample Date	Depth Below Grade (feet)	Naphthalene	Phenanthrene	Pyrene	Acenaphthene	Acenaphthylene	Anthracene	Benzo(a) anthracene	Chrysene	Fluoranthene	Fluorene	Total PAH
DUP-1													
	5/18/2005		290,000	65,000	35,000	25,000	8,900	16,000	9,200	7,100	23,000	17,000	496,200
IP-1													
	5/18/2005	12-14	440,000	92,000	50,000	34,000	22,000	22,000	12,000	11,000	34,000	26,000	743,000
	6/13/2006	12-14	140,000	32,000	19,000	12,000 U	12,000 U	12,000 U	12,000 U	12,000 U	12,000 U	12,000 U	233,000
	5/18/2005	14-16	500,000	120,000	90,000	46,000	8,200	29,000	21,000	19,000	55,000	28,000	916,200
	6/13/2006	14-16	200,000	52,000	29,000 U	29,000 U	29,000 U	29,000 U	29,000 U	29,000 U	29,000 U	29,000 U	368,000
IP-2													
	5/18/2005	10-12	1,100,000	470,000	240,000	110,000	130,000	96,000	55,000	51,000	150,000	140,000	2,542,000
	6/13/2006	10-12	520,000	150,000	94,000	61,000 U	61,000 U	61,000 U	61,000 U	61,000 U	61,000 U	61,000 U	977,500
	5/18/2005	12-14	1,600,000	570,000	300,000	69,000	230,000	120,000	62,000	58,000	200,000	170,000	3,379,000
	6/13/2006	12-14	370,000	110,000	72,000	58,000 U	58,000 U	58,000 U	58,000 U	58,000 U	58,000 U	58,000 U	755,000
IP-3													
	5/18/2005	12-14	410,000	140,000	71,000	38,000	39,000	29,000	16,000	15,000	46,000	42,000	846,000
	6/13/2006	12-14	260,000	100,000	59,000	30,000 U	30,000 U	30,000 U	30,000 U	30,000 U	32,000	34,000	560,000
	5/18/2005	14-16	280,000	75,000	41,000	32,000	5,900	18,000	10,000	9,000	28,000	21,000	519,900
	6/13/2006	14-16	570,000	170,000	90,000	58,000 U	66,000	58,000 U	58,000 U	58,000 U	58,000 U	58,000 U	1,070,000
MP-1													
	5/18/2005	12-14	980,000	250,000	140,000	36,000	120,000	62,000	35,000	34,000	92,000	73,000	1,822,000
	6/13/2006	12-14	300,000	64,000	37,000	29,000 U	29,000 U	29,000 U	29,000 U	29,000 U	29,000 U	29,000 U	502,500
	5/18/2005	14-16	340,000	94,000	50,000	16,000	39,000	22,000	12,000	11,000	36,000	25,000	645,000
	6/13/2006	14-16	240,000	45,000	30,000 U	30,000 U	30,000 U	30,000 U	30,000 U	30,000 U	30,000 U	30,000 U	405,000
MP-2													
	6/13/2006	12-14	420,000	86,000	60,000 U	60,000 U	60,000 U	60,000 U	60,000 U	60,000 U	60,000 U	60,000 U	746,000
	6/13/2006	14-16	310,000	48,000	30,000	28,000 U	28,000 U	28,000 U	28,000 U	28,000 U	28,000 U	28,000 U	486,000
MP-3													
	5/18/2005	12-14	360,000	99,000	52,000	52,000	9,000	23,000	13,000	12,000	35,000	27,000	682,000
	6/13/2006	12-14	160,000	40,000	23,000	20,000	12,000 U	12,000 U	12,000 U	12,000 U	12,000	13,000	292,000
	5/18/2005	14-16	300,000	69,000	37,000	29,000	8,100	17,000	9,200	9,400	26,000	19,000	523,700
	6/13/2006	14-16	670,000	140,000	85,000	71,000	57,000 U	57,000 U	57,000 U	57,000 U	57,000 U	57,000 U	1,137,000
MP-4													
	5/18/2005	13.5-14.5	1,400,000	320,000	170,000	160,000	25,000	80,000	51,000	38,000	130,000	88,000	2,462,000
	6/13/2006	13.5-14.5	270,000	50,000	34,000	26,000	15,000 U	15,000 U	15,000 U	15,000 U	18,000	16,000	444,000

Notes:

PAH = Polycyclic Aromatic Hydrocarbons
Dup = duplicate
Concentrations are reported in micrograms per kilogram (ug/Kg) or parts per billion (ppb).
U = compound was not detected at the indicated concentration
Compounds with a "U" flag are reported at their reporting limits.
Total PAH value includes one half the reporting limits for compounds associated with a "U" flag.
Only compounds observed at the Site on a consistent basis are presented.

Table 5-4
BTEX Results for Composite Soil Samples

Boring	Sample Date	Depth Below Grade (feet)	Benzene	Toluene	Ethylbenzene	Xylene	Total BTEX
DUP-1							
	5/18/2005		140 U	4,300	22,000	45,000	71,370
IP-1							
	5/18/2005	12-14	1,000	56,000	110,000	220,000	387,000
	6/13/2006	12-14	1,900 U	34,000	74,000	140,000	248,950
	5/18/2005	14-16	590 U	29,000	84,000	160,000	273,295
	6/13/2006	14-16	4,900 U	44,000	140,000	250,000	436,450
IP-2							
	5/18/2005	10-12	4,200	64,000	82,000	150,000	300,200
	6/13/2006	10-12	3,100 U	21,000	100,000	180,000	302,550
	5/18/2005	12-14	8,000	96,000	100,000	200,000	404,000
	6/13/2006	12-14	3,100 U	51,000	86,000	160,000	298,550
IP-3							
	5/18/2005	12-14	380 U	26,000	68,000	140,000	234,190
	6/13/2006	12-14	200 U	1,800	4,200	11,000	17,100
	5/18/2005	14-16	190 U	3,800	27,000	59,000	89,895
	6/13/2006	14-16	2,800 U	55,000	84,000	190,000	330,400
MP-1							
	6/13/2006	12-14	1,600 U	18,000	65,000	120,000	203,800
	5/18/2005	14-16	4,000	58,000	51,000	120,000	233,000
	6/13/2006	14-16	1,500 U	33,000	55,000	100,000	188,750
MP-2							
	6/13/2006	12-14	2,900 U	43,000	95,000	180,000	319,450
	6/13/2006	14-16	1,700 U	17,000	56,000	110,000	183,850
MP-3							
	5/18/2005	12-14	140 U	5,000	24,000	55,000	84,070
	6/13/2006	12-14	1,400 U	4,900	43,000	100,000	148,600
	5/18/2005	14-16	160 U	5,400	28,000	56,000	89,480
	6/13/2006	14-16	1,600 U	12,000	61,000	130,000	203,800
MP-4							
	6/13/2006	13.5-14.5	3,400 U	57,000	120,000	220,000	398,700

Notes:

BTEX = Benzene, Toluene, Ethylbenzene and Xylene
Dup = duplicate
Concentrations are reported in micrograms per kilogram (ug/Kg) or parts per billion (ppb).
U = compound was not detected at the indicated concentration
Compounds with a "U" flag are reported at their reporting limits.
Total BTEX value includes one half the reporting limits for compounds associated with a "U" flag.

Table 5-5
PAH Results for Grab Soil Samples

Boring	Sample Date	Depth Below Grade (feet)	Naphthalene	Phenanthrene	Pyrene	Acenaphthene	Acenaphthylene	Anthracene	Benzo(a) anthracene	Chrysene	Fluoranthene	Fluorene	Total PAH
IP-1													
	5/18/2005	12-14	700,000	150,000	79,000	51,000	46,000	37,000	18,000	17,000	56,000	44,000	1,198,000
	6/13/2006	12-14	500,000	98,000	67,000	58,000 U	58,000 U	58,000 U	58,000 U	58,000 U	58,000U	58,000 U	868,000
IP-2													
	5/18/2005	12-14	1,500,000	560,000	290,000	56,000	240,000	110,000	63,000	60,000	200,000	160,000	3,239,000
	6/13/2006	12-14	350,000	100,000	66,000	54,000 U	54,000 U	54,000 U	54,000 U	54,000 U	54,000U	54,000 U	705,000
MP-1													
	5/18/2005	12-14	1,000,000	250,000	140,000	48,000	100,000	57,000	31,000	27,000	92,000	72,000	1,817,000
	6/13/2006	12-14	370,000	83,000	58,000 U	58,000 U	58,000 U	58,000 U	58,000 U	58,000 U	58,000U	58,000 U	685,000
MP-2													
	6/13/2006	12-14	580,000	110,000	73,000	58,000 U	58,000 U	58,000 U	58,000 U	58,000 U	58,000U	58,000 U	966,000
MP-3													
	5/18/2005	12-14	280,000	70,000	36,000	36,000	5,900	17,000	9,700	8,500	25,000	19,000	507,100
	6/13/2006	12-14	420,000	96,000	59,000	54,000 U	54,000 U	54,000 U	54,000 U	54,000 U	54,000U	54,000 U	764,000

Notes:

PAH = Polycyclic Aromatic Hydrocarbons
Dup = duplicate
Concentrations are reported in micrograms per kilogram (ug/Kg) or parts per billion (ppb).
U = compound was not detected at the indicated concentration
Compounds with a "U" flag are reported at their reporting limits.
Total PAH value includes one half the reporting limits for compounds associated with a "U" flag.
Only compounds observed at the Site on a consistent basis are presented.

Table 5-6
BTEX Results for Grab Soil Samples

Boring	Sample Date	Depth Below Grade (feet)	Benzene	Toluene	Ethylbenzene	Xylene	Total BTEX
IP-1							
	5/18/2005	12-14	520 U	56,000	100,000	210,000	366,260
	6/13/2006	12-14	3,000 U	62,000	100,000	200,000	363,500
IP-2							
	5/18/2005	12-14	17,000	200,000	160,000	370,000	747,000
	6/13/2006	12-14	1,700 U	40,000	56,000	110,000	206,850
MP-1							
	5/18/2005	12-14	3,400	62,000	71,000	140,000	276,400
	6/13/2006	12-14	3,100 U	20,000	91,000	160,000	272,550
MP-2							
	6/13/2006	12-14	3,100 U	84,000	130,000	250,000	465,550
MP-3							
	5/18/2005	12-14	190 U	6,400	27,000	58,000	91,495
	6/13/2006	12-14	1,400 U	4,700	42,000	93,000	140,400

Notes:

BTEX = Benzene, Toluene, Ethylbenzene and Xylene
Concentrations are reported in micrograms per kilogram (ug/Kg) or parts per billion (ppb).
U = compound was not detected at the indicated concentration
Compounds with a "U" flag are reported at their reporting limits.
Total BTEX value includes one half the reporting limits for compounds associated with a "U" flag.

Table 5-7
PAH SPLP Results for Composite Soil Samples

Boring	Sample Date	Depth Below Grade (feet)	Naphthalene	Phenanthrene	Pyrene	Acenaphthene	Acenaphthylene	Anthracene	Benzo(a) anthracene	Chrysene	Fluoranthene	Fluorene	Total PAH
IP-1													
	5/18/2005	12-14	4,900	260	500 U	140	160	100 U	100 U	100 U	100 U	100 U	5,960
	6/13/2006	12-14	1,600	330 U	330 U	330 U	330 U	330 U	330 U	330 U	330 U	330 U	3,085
	6/13/2006	14-16	1,600	330 U	330 U	330 U	330 U	330 U	330 U	330 U	330 U	330 U	3,085
IP-2													
	6/13/2006	10-12	1,800	320	170 U	170 U	170 U	170 U	170 U	170 U	170 U	170 U	2,800
	5/18/2005	12-14	3,900	280	250 U	64	280	50 U	50 U	50 U	96	88	4,908
	6/13/2006	12-14	1,600	330 U	330 U	330 U	330 U	330 U	330 U	330 U	330 U	330 U	3,085
MP-1													
	5/18/2005	12-14	6,200	600	400 U	130	460	120	80 U	80 U	250	190	8,230
	6/13/2006	12-14	1,300	170 U	170 U	170 U	170 U	170 U	170 U	170 U	170 U	170 U	2,065
	6/13/2006	14-16	1,200	170 U	170 U	170 U	170 U	170 U	170 U	170 U	170 U	170 U	1,965
MP-2													
	6/13/2006	12-14	1,500	330 U	330 U	330 U	330 U	330 U	330 U	330 U	330 U	330 U	2,985
MP-3													
	5/18/2005	12-14	4,800	160	500 U	190	100 U	100 U	100 U	100 U	100 U	100 U	5,700
	6/13/2006	12-14	600	120	83 U	83 U	83 U	83 U	83 U	83 U	83 U	83 U	1,052
	6/13/2006	14-16	1,400	330 U	330 U	330 U	330 U	330 U	330 U	330 U	330 U	330 U	2,885

Notes:

SPLP = Synthetic Precipitate Leaching Procedure
PAH = Polycyclic Aromatic Hydrocarbons
Concentrations are reported in micrograms per liter (ug/L) or parts per billion (ppb).
U = compound was not detected at the indicated concentration
Compounds with a "U" flag are reported at their reporting limits.
Total PAH value includes one half the reporting limits for compounds associated with a "U" flag.

Table 5-8
BTEX SPLP Results for Composite Soil Samples

Boring	Sample Date	Depth Below Grade (feet)	Benzene	Toluene	Ethylbenzene	Xylene	Total BTEX
IP-1							
	5/18/2005	12-14	100 U	1,100	1,900	3,570	6,620
	6/13/2006	12-14	100 U	720	1,800	3,400	5,970
	6/13/2006	14-16	100 U	1,100	2,200	4,300	7,650
IP-2							
	5/18/2005	10-12	100 U	1,100	1,900	3,570	6,620
	6/13/2006	10-12	100 U	200	810	1,500	2,560
	6/13/2006	12-14	100 U	870	1,500	2,700	5,120
MP-1							
	5/18/2005	12-14	100 U	1,800	1,500	2,780	6,130
	6/13/2006	12-14	100 U	520	1,800	2,800	5,170
	6/13/2006	14-16	100 U	910	1,600	2,700	5,260
MP-2							
	6/13/2006	12-14	100 U	1,300	1,600	3,300	6,250
MP-3							
	5/18/2005	12-14	25 U	96	570	1,300	1,979
	6/13/2006	12-14	100 U	100 U	590	1,300	1,990
	6/13/2006	14-16	100 U	440	1,700	3,400	5,590

Notes:

SPLP = Synthetic Precipitate Leaching Procedure
BTEX = Benzene, Toluene, Ethylbenzene and Xylene
Concentrations are reported in micrograms per liter (ug/L) or parts per billion (ppb).
U = compound was not detected at the indicated concentration
Compounds with a "U" flag are reported at their reporting limits.
Xylene concentrations for 5/18/2005 data is calculated as the sum of m,p-xylenes and o-xylenes.
Total BTEX value includes one half the reporting limits for compounds associated with a "U" flag.

Grab Soil Sample Results

Grab soil sample collection techniques are often used when assessing remedial system performance for data presentation to regulatory agencies. Grab samples lend themselves well to statistical analysis if sufficient quantities of samples are collected. However, grab samples (especially if limited in number) from a highly variable contaminant concentration treatment area can provide a false indication of remedial system performance. It was decided that within this field demonstration both grab and composite soil sampling would be performed for comparison of the two techniques. Baseline and post-application grab samples were collected at a single vertical interval at four locations (IP-1, IP-2, MP-1, and MP-3) within the target treatment area and analyzed for PAHs and BTEX compounds. TPH was not assessed. The sample analyses results are presented in Tables 5-5 and 5-6 and Figure 5-8. The following is a brief comparison of the baseline and post-application results for the grab soil samples:

- Total PAHs concentration decreased in three of the four sample sets, with an increase in the fourth set. The overall average decrease in PAH concentrations was approximately 55 percent.
- Total BTEX concentration decreased at the same three of four locations where PAH decreases were measured, and with an increase in the fourth location. The overall average decrease in BTEX concentrations was approximately 34 percent.

Composite Soil Sample SPLP Results

SPLP is an EPA standard method designed to measure the leaching characteristic of organic contaminants from the soil into groundwater. An SPLP analysis for PAHs and BTEX compounds was performed for baseline and post-application soil samples collected from a single vertical interval at four locations (IP-1, IP-2, MP-1, and MP-3) within the field demonstration area. TPH was not assessed. The results of the SPLP comparative data analysis are presented in Tables 5-7 and 5-8 and Figure 5-9, and are briefly summarized below:

- Total PAHs: SPLP concentrations for total PAHs decreased at all four sample locations due to treatment with activated persulfate. The average decrease was by approximately 63 percent; and
- Total BTEX: Similarly, the SPLP for BTEX decreased at all four sample locations after treatment with activated persulfate, with an average decrease of approximately 26 percent.

Soil Sample Results Discussion

An average decrease of 55 percent and 68 percent were observed in the paired PAH and TPH data, respectively, as a result of the single application of activated persulfate; whereas no significant change was observed in the average BTEX data (four percent increase). The decreases observed in the average PAH and TPH data is in agreement with bench test results where 40 to 60 percent reductions in TPH and PAH concentrations were measured. With minimal exception (two composite BTEX samples), the contaminants measured in soil samples behaved in a similar manner whether collected as a grab or composite sample (i.e., the concentration of each of the COCs either increasing or decreasing in the same sample). The data indicates that the majority of the locations received treatment, while others may have received little to no treatment by the application (as indicated by the magnitude of the increases). The increasing contaminant trend found in the grab sample from 12 to 14 feet bgs at MP-3 is counter to the decreasing trend found in the composite sample of the same interval. This highlights the potential issue with using grab samples, and illustrates how they can provide specific data about a small subsection of soil while the overall impact on the rest of the soil may be different.

Data Evaluation

The objectives of the data analyses performed on the baseline and post-application soil and SPLP data were:

- Determine if a statistically significant difference exists between the baseline and post-application contaminant impacts on soil and in the SPLP data;
- Quantify the performance of the application of the alkaline-activated persulfate within the target soil volume relative to the endpoint expectations as developed from the bench-scale testing; and,
- Assess the overall effectiveness of the ISCO application within and beyond the target treatment area.

To accomplish these objectives, a non-parametric statistical analysis was performed to establish the independence of the data sets (i.e., does the data support a statistical significance between the data sets); and a spatially-weighted mass estimate was developed to calculate the mass of BTEX, PAHs and TPH within and in the vicinity of the target treatment volume prior to and following the field demonstration.

Statistical Analysis of the Data

The Wilcoxon Signed-Rank test, a non-parametric statistical test, was used with the data sets to determine the independence of the baseline and post-application results. The baseline soil sampling data for PAH, BTEX, TPH, SPLP PAH, and SPLP BTEX were compared against the post-application laboratory results for all paired samples (i.e., locations that have both baseline and post-injection results from the same depth interval).

The analysis indicates that the medians for the baseline and post-application sampling were statistically different (at a 90 percent confidence level) for all sample classes presented above, except for the composite BTEX samples. The composite BTEX data analyses results suggest that the treatment demonstrated little to no effect on the BTEX concentrations.

Theissen Polygon Analysis

A Theissen Polygon analysis was performed to convert the measured baseline and post-application soil contaminant concentrations to an estimated contaminant mass. A Theissen Polygon analysis spatially weights soil sample COC results to provide an estimate of COC mass over a given soil volume.

Data indicate (Table 5-2) that there is a significant reduction of total contaminant mass not only within but also outside of the target treatment soil volume, at MP-4. To evaluate this further, a Theissen Polygon analysis was conducted to estimate both the baseline and post-application mass of total PAHs, total BTEX, and TPH based on using the results of the composite soil samples both within and outside of the target treatment area.

Two potential treatment zones with areas of 100 and 160 square feet were considered for the analysis (Figure 5-10). For each treatment area, the contaminant soil concentration at each of the relevant sampling locations and depth intervals were converted to a contaminant mass for the associated area of influence. Table 5-9 presents a summary of calculated masses of total PAHs, total BTEX and TPH from composite samples, and the percent change in mass due to the activated persulfate application. Table 5-10 summarizes the comparative mass increases and decreases, and indicates that for the PAH and TPH data, the mass decrease (due to 9 of the 11 samples showing decreased concentrations) is significantly higher than mass increase (based on data from the other two sampling intervals). Table 5-11 presents the mass calculated for each sampling interval based on the composite soil sampling data.

Figure 5-10
Treatment Zones for Theissen Polygon Analysis

The results of the analyses (Table 5-10 and Figure 5-11) indicate that the estimated COC mass in the initial target area (approximately 100 square feet) decreased in PAH and TPH by approximately 49 and 63 percent, respectively, and increased in BTEX mass by approximately two percent. If the data from MP-4 and an area outside the original target area is also considered (approximately 160 square feet), the estimated mass of PAHs and TPH decreased by approximately 63 and 75 percent, respectively, and BTEX mass decreased by approximately one percent. It should again be noted that the pre and post application BTEX data sets were not found to be statistically different.

Table 5-9
Theissen Polygon Analysis: Contaminant Mass Summary

Treatment Areas	Total PAHs			Total BTEX			TPH		
	Baseline (Kg)	Post-Application (Kg)	Percent Change in Mass (%)[1]	Baseline (Kg)	Post-Application (Kg)	Percent Change in Mass (%)[1]	Baseline (Kg)	Post-Application (Kg)	Percent Change in Mass (%)[1]
Control Area 1 [2]	37.4	18.9	49%	6.84	6.95	-2%	118	44	63%
Control Area 2 [3]	75.3	27.5	63%	8.04	7.99	1%	276	68	75%

Notes:

Theissen Polygon method is commonly used for environmental data analysis without introducing bias

[1] A negative number indicates an overall increase in contaminant mass

[2] Original treatment zone of 10 feet x 10 feet area

[3] Includes MP-4 to create a treatment zone of 10 feet x 16 feet area

PAHs = Polycyclic Aromatic Hydrocarbons

BTEX = Benzene, Toluene, Ethylbenzene and Xylene

TPH = Total Petroleum Hydrocarbons

Kg = kilograms

Table 5-10
Theissen Polygon Analysis: Mass Increases vs. Decreases

Treatment Areas	Total PAHs			Total BTEX			TPH		
	Mass Increase (Kg)	Mass Decrease (Kg)	Total Change in Mass [1] (Kg)	Mass Increase (Kg)	Mass Decrease (Kg)	Total Change in Mass [1] (Kg)	Mass Increase (Kg)	Mass Decrease (Kg)	Total Change in Mass [1] (Kg)
Control Area 1 [2]	3.4	22.0	18.6	1.81	1.70	-0.11	2.0	76.0	74.0
Control Area 2 [3]	3.4	51.2	47.8	1.88	1.93	0.05	2.0	210.4	208.4

Notes:

[1] A negative number indicates an overall increase in contaminant mass

[2] Original treatment zone of 10 feet x 10 feet area

[3] Includes MP-4 to create a treatment zone of 10 feet x 16 feet area

PAHs = Polycyclic Aromatic Hydrocarbons

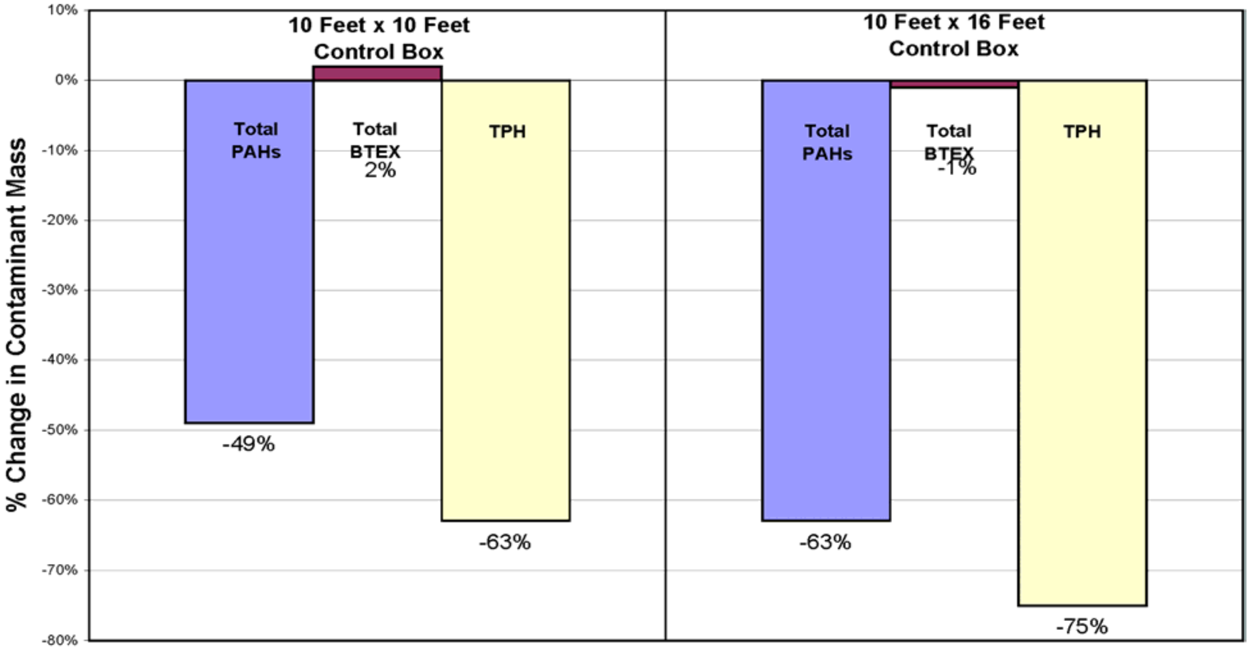
BTEX = Benzene, Toluene, Ethylbenzene and Xylene

TPH = Total Petroleum Hydrocarbons

Kg = kilograms

Table 5-11
Theissen Polygon Analysis: COC Mass Calculation

Treatment Areas	Boring	Representative Depth Below Grade (feet)	Total PAHs (kg)			Total BTEX (kg)			TPH (kg)		
			Baseline	Post	Difference[1]	Baseline	Post	Difference[1]	Baseline	Post	Difference[1]
Control Area 1 [2]	IP-1	11-14	3.43	1.08	*2.36*	1.79	1.15	*0.64*	19.86	2.54	*17.32*
		14-16	2.82	1.13	*1.69*	0.84	1.34	*-0.50*	13.86	2.52	*11.33*
	IP-2	11-14	10.10	3.88	*6.21*	1.19	1.20	*-0.01*	24.23	8.34	*15.89*
		14-16	8.95	2.00	*6.95*	1.07	0.79	*0.28*	16.95	4.77	*12.18*
	IP-3	11-14	2.94	1.94	*0.99*	0.81	0.06	*0.75*	9.72	2.57	*7.15*
		14-16	1.20	2.48	*-1.27*	0.21	0.77	*-0.56*	6.25	7.18	*-0.93*
	MP-1	11-14	2.12	0.58	*1.54*	-	-	-	5.35	1.51	*3.84*
		14-16	0.50	0.31	*0.19*	0.18	0.15	*0.03*	0.93	0.55	*0.38*
	MP-3	11-14	3.59	1.54	*2.06*	0.44	0.78	*-0.34*	14.23	6.32	*7.91*
		14-16	1.84	4.00	*-2.15*	0.31	0.72	*-0.40*	7.03	8.08	*-1.05*
Total Contaminant Mass (Kg)			**37.49**	**18.95**	***18.55***	**6.85**	**6.96**	***-0.11***	**118.41**	**44.39**	***74.02***
Control Area 2 [3]	IP-1	11-14	3.86	1.21	*2.65*	2.01	1.29	*0.72*	22.32	2.86	*19.47*
		14-16	3.17	1.27	*1.90*	0.95	1.51	*-0.56*	15.57	2.84	*12.74*
	IP-2	11-14	11.55	4.44	*7.11*	1.36	1.38	*-0.01*	27.72	9.54	*18.18*
		14-16	10.24	2.29	*7.95*	1.22	0.90	*0.32*	19.39	5.45	*13.94*
	IP-3	11-14	2.94	1.94	*0.99*	0.81	0.06	*0.75*	9.72	2.57	*7.15*
		14-16	1.20	2.48	*-1.27*	0.21	0.77	*-0.56*	6.25	7.18	*-0.93*
	MP-1	11-14	8.41	2.32	*6.09*	-	-	-	21.25	6.00	*15.24*
		14-16	1.99	1.25	*0.74*	0.72	0.58	*0.14*	3.69	2.19	*1.51*
	MP-3	11-14	3.59	1.54	*2.05*	0.44	0.78	*-0.34*	14.22	6.32	*7.90*
		14-16	1.84	3.99	*-2.15*	0.31	0.72	*-0.40*	7.02	8.07	*-1.05*
	MP-4	11-16	26.53	4.78	*21.75*	-	-	-	129.32	15.09	*114.23*
Total Contaminant Mass (Kg)			**75.32**	**27.52**	***47.80***	**8.04**	**7.99**	***0.05***	**276.48**	**68.11**	***208.37***



Note:
Negative scale indicates a net reduction in contaminant mass.

Figure 5-11
Change in Site Contaminant Mass Based on Composite Soil Samples

The data indicate a significant mass reduction in the PAHs and TPH (equal to or greater than 49 percent) within the area treated by activated persulfate. The slight increase in estimated mass of BTEX compounds is indicative of little to no change in BTEX mass due to the treatment with alkaline persulfate. This result is counter to previous applications by XDD that show activated persulfate is able to successfully degrade BTEX compounds at the bench- and full-scale. While the reason for the insignificant change in BTEX concentrations is unknown, it is hypothesized that the BTEX may be tied up in the less readily available organics and that any BTEX in the readily oxidizable organics was likely flushed or degraded from the area prior to the demonstration.

Field Application Summary

Approximately 3,000 gallons of 250 g/L activated sodium persulfate solution was injected through five injection locations within a 10-foot-by-10-foot target area and a five-foot vertical interval. The performance monitoring data gathered at the time of the ISCO application indicates that aquifer conditions favored the alkaline activation of sodium persulfate and that the impacts of the application extended well beyond the targeted treatment area. The data also indicates that a significant mass of TPH and PAHs was degraded while the BTEX mass was essentially unaffected. The following is a summary of the field demonstration results:

- The mass PAHs and TPH destroyed from a single application of activated persulfate was in the range of 40 to 60 percent, as expected based on the bench-scale test results for the Laurel Street soils.
- Statistically, the mass of BTEX did not appear to change due to the activated persulfate application. This result is counter to what was expected, and is believed to be due to the availability of the BTEX for oxidation in the site soils. It is hypothesized that the BTEX may be tied up in the less readily available organics and that any BTEX in the readily oxidizable organics was likely flushed or degraded from the area prior to the demonstration.
- Following treatment, the leachability of PAHs and BTEX compounds was decreased. PAH SPLP decreased by approximately 63 percent and the BTEX SPLP was reduced by 26 percent;
- Site heterogeneities and clayey soils likely impacted the distribution of the reagents at two of 11 sample pairs (IP-3 14 to 16 feet bgs, and MP-3 14 to 16 feet bgs), which appear to not have received treatment during the ISCO application. Subsurface heterogeneity is a common problem that is discussed in Section 6;
- Based on the calculated contaminant mass reduction (in control areas 1 and 2) and persulfate mass application, the oxidant loading rate was approximately 14 to 38 pounds of sodium persulfate per pound of TPH degradation, and approximately 59 to 153 pounds of sodium persulfate per pound of PAHs degradation in the contaminant matrix found at the site; and,
- NAPL mobilization and accumulation were not observed during the activated persulfate field application at this site.

6

ISCO AT MGP SITES: A FEASIBILITY FRAMEWORK

The general guidance principles provided in this section of the report are based on the information developed as part of this demonstration project and on experiences gained by XDD and others in the application of ISCO at both MGP and non-MGP sites.

ISCO has been researched and applied in the field for over 15 years and has developed into a technically complex yet promising technology when designed and applied correctly for the remediation of sites impacted with a wide range of contaminants. ISCO has several beneficial characteristics that have resulted in its selection as a remedial technology of choice at MGP sites. The primary beneficial characteristics include:

- ISCO technologies can degrade the wide suite of constituents found within MGP residuals;
- The degradation can occur *in situ*, so that contaminated soils do not have to be excavated;
- ISCO often proves to be cost-effective relative to the typical alternatives available, especially for areas that are inaccessible or too deep to consider excavation and treatment off-site;
- ISCO reactions occur relatively rapidly, on the order of hours to months, dependent on the oxidant demand and conditions associated with the target treatment area including soil type, stratigraphy, lithology; and,
- With MGP residuals, ISCO using sodium persulfate (and also permanganate) has been observed to decrease the leaching characteristics of the treated soils, as was illustrated in this field demonstration project.

While there are potential benefits associated with ISCO, it should not be considered a universal remedy for every MGP site. ISCO, as will be discussed further in this section, may be limited by several factors, many of which revolve around the ability to achieve effective contact between the oxidant and the targeted mass of MGP residuals.

This section of the report has been subdivided into three discussions topics: site screening guidance, ISCO application guidance (including common issues that may cause failure of the technology to achieve the endpoint objectives), and ISCO cost of application guidance. The information presented herein has been written with intention to assist MGP site managers in screening sites for the most appropriate ISCO technology.

Site Screening for ISCO

Whether or not ISCO is an appropriate remedial option for a specific site depends largely upon two factors:

- Site conditions; and,
- Remedial goals for the site.

Site Conditions

Every site is unique with its own technical and non-technical challenges, problems, and issues that need to be resolved. Several subsurface characteristics are critical to the application of ISCO; these include soil type, hydraulic conductivity, and soil heterogeneity. The non-target demand for the oxidant exerted by the site soil and the impact of groundwater flow on contact time may play a role in the resulting geochemistry when using persulfate. Also critical to the ISCO design and success are site-specific factors such as the contaminant type, contaminant(s) masses, and the phase (dissolved, sorbed, residual and NAPL) and distribution of each contaminant. Issues associated with each of these are briefly discussed in Table 6-1.

Table 6-1
Site Screening Guidance: Common Site Issues for ISCO

Category	Characteristics	Common Issues with ISCO Technologies
Soil	Heterogeneity	Heterogeneity in the subsurface can impact any of the following soil characteristics creating multiple environments to be treated in very close proximity. The most common example is different conductive zones which result in preferential flow paths and uneven distribution of the reagents.
	Type	Type of soil usually is related to many other of the soil factors listed in this table. In general, clays are the most difficult to treat and conductive soils, such as sands and gravels are most readily treated. Accommodations can be made for most soil types, although cost will typically increase with the degree of difficulty of the application.
	Porosity	Porosity directly impacts the volume of reagent required to fill/treat a volume of soil. Porosity can impact injection times, radius of influence from each injection point, and oxidant loading.
	Hydraulic Conductivity	Decreasing hydraulic conductivities decrease injection rates which can increase injection times and project costs and even impact the selection of ISCO technologies.
	Non-Target Demand for Oxidant	Organic matter, reduced metals and other certain mineralogies (e.g. surface area) will react with the oxidants increasing the mass, and cost, of oxidant required to treat a given area.
	Geochemistry	Mineralogies can interact with certain oxidants. Common examples include high organic carbon zones interfering with permanganate due to very high non-target oxidant demand, or carbonates interfering with catalyzed hydrogen peroxide due to a scavenging reaction with the hydroxyl radical.
Groundwater	Flow	High groundwater flow rates can decrease the contact time between the reagents and the contaminant. The North Water Street site is an example of this condition.
	Preferential Flow Paths	Similar to heterogeneity impacts on soils, similar soils can have preferential flow paths that will impact reagent distribution. An example would be cracks and fissures that can be found in clays.
Contaminants	Type	Type of contaminant can impact oxidant selection, activation method and other design considerations for an ISCO technology. Hydrogen peroxide, sodium persulfate and ozone based technologies are most likely to be applied to contaminants typical of MGP residuals.
	Mass	As ISCO technologies work on a direct reaction between an oxidant and a contaminant, as the mass of contaminant increases so does the mass of oxidant (and associated cost). Therefore, the accuracy of a mass estimate and location of mass can be critical for a successful ISCO application.
	Phase	ISCO technologies need to contact the contaminant. Thus the phase of the contamination, aqueous, sorbed to soils or in a NAPL phase, impacts the ability to achieve that contact. In general, ISCO technologies work best for contamination in the aqueous, sorbed, residual and small lenses of NAPL phases. Certain oxidants only react in the aqueous phase, in which case the effectiveness of ISCO could be dissolution or desorption limited.
Site Limitations	Visibility	The visibility of a site to the public or others may create issues that impact the selection of the oxidant, method of application, and other design considerations.
	Access	Access issues are commonly associated with physical limitations caused by structures, natural features, active facilities or property issues. Many of these can be addressed with the selection of technologies and ISCO application design. For example, activated persulfate is generally better suited for applications under buildings as its stability allows for fewer injection locations and it typically generates less heat and gas.
	Structures	In addition to the issues associated with structures and access, the reactivity of ISCO reagents and certain structures can become important. Areas of concern include metal pipes or other structures that could corrode.

Site Remedial Goals

Remedial goals may vary from site to site based on several factors including regulatory requirements, site remedial strategy (e.g., ISCO followed by bioremediation) and other factors. For example, remedial goals may include decreases in:

- contaminant concentrations measured in grab or composite soil samples,
- contaminant concentrations in groundwater (mass flux reduction), and,
- visual contamination, such as NAPL,

Due to the high variability in concentrations of MGP residuals found in site soils, composite soil samples are considered more representative of the impacts over a given soil volume and are usually preferable to grab soil samples when evaluating ISCO performance.

ISCO is a mass reduction technology that is dependent primarily on the contaminants dissolving into the aqueous phase for treatment. Due to the hydrophobic nature of most MGP residuals, a vast majority of the contaminant mass is typically found in soil rather than groundwater. This phenomenon makes contaminant concentrations found in soil samples a significantly better metric than contaminant concentrations in groundwater samples to evaluate the effectiveness of an ISCO application in reducing contaminant mass.

In addition, for many *in situ* mass reduction technologies it is possible to greatly reduce the mass of a contaminant in the soil and not see a significant change in the measured impact in groundwater concentrations, due to partitioning processes. This phenomenon also depends on the architecture of the contaminant distribution. Contaminants distributed primarily in residual or sorbed phase in the soils are typically readily contacted and treated with oxidant. However, contaminants distributed in NAPL lenses where the pore spaces are filled with NAPL have limited mass transfer into the aqueous phase for treatment. One of the apparently unique aspects of ISCO that has been measured using both sodium persulfate and permanganate (this observation is based on a limited number of studies) is the potential formation of precipitants or a film over the NAPL that can reduce the mass transfer from the NAPL-filled pores into the groundwater, resulting in a reduction in the groundwater mass flux that is disproportionate to the mass reduction in the NAPL.

An ISCO technology may often be applied multiple times to a site in order to achieve stringent endpoint goals. While not always the case, each subsequent application has the potential to be less effective than the previous application as less contamination is readily available. For example, if a site has a mass of 10,000 mg/Kg TPH with a remedial goal of 1 mg/Kg TPH, and 80 percent of TPH is degraded in each application, it would take approximately six applications to achieve the remedial goal. However, if the degradation efficiency decreased by five percent after each application (80, 75, 70, etc.) then approximately 11 applications would be required to achieve the remedial goal of 1 mg/Kg.

ISCO Site Selection

Based on the factors described in this section, ISCO is more likely to be an applicable, cost-effective, remedial alternative at sites where:

- Soils are permeable enough (sands and silty sands) to allow for the injection and distribution of the reagents;
- The contamination is present in phases ranging from aqueous to residual to small (e.g., less than a few inches) layers of NAPL filled pores;
- ISCO is to be used primarily for mass or mass flux reduction. (The action of the oxidant to create a reduction in the mass transfer at the NAPL surface into groundwater is limited);
- The remedial goal can be achieved with a mass reduction, as measured by composite soil samples, of one and possibly up to two orders of magnitude; and,
- The remedial goal is to significantly decrease (greater than 75%) the mass flux in the groundwater (dependent on the contaminant architecture as discussed in this section).

Conversely, ISCO is less likely to be an applicable remedial alternative at sites where:

- The non-target oxidant demand as measured by COD is high (e.g., greater than 20,000 mg/Kg or 2 percent) as to render the project too expensive and impractical. This is dependent on the site remedial goal, the costs, and practicality of the ISCO application and may be best determined through a limited bench-scale test;
- The MGP residuals are primarily located in clay or dense silts with low hydraulic conductivity;
- The site geochemistry severely impedes the use of an ISCO technology (e.g., soil mineralogy that either contains excess carbonates or transition metals can eliminate the use of peroxide-based ISCO);
- Due to a high degree of heterogeneity in the soils and rapid groundwater movement, adequate contact or contact time (ranging from four days to 60 days for activated persulfate, based on the soil desorption characteristics as described in Section 1 of this report) can not be established (Note: a continuous versus a batch oxidant injection approach may be considered under rapid groundwater flow conditions);
- The remedial goal requires greater than a one to two order of magnitude decrease in the mass of contaminants, or requires NAPL phase destruction for layers greater than a few inches in thickness; and/or,
- The contamination is readily accessible or otherwise amenable to another, less expensive, remedial technology (typically considered to be excavation of impacted shallow soils).

These guidelines are intended to provide a general overview as to what defines a good or bad candidate site for ISCO persulfate. It should be noted that the technology, both in terms of science and implementation, continues to evolve at a rapid pace (e.g., surfactant enhancements to accelerate mass transfer into the aqueous phase). Most of the limitations of its use are due to rapidly increasing costs. Certain sites may exist where the costs become less relevant because ISCO may be engineered to be effective.

ISCO Strategy Development

The use of ISCO technologies in the treatment of subsurface contamination has grown rapidly in recent years as a result of the perceived advantages, as presented in Section 1 of this report. Several specific ISCO technologies have been developed which have protocols. This subsection will provide a brief overview of these ISCO technologies as they pertain to MGP sites and the evolution of an ISCO project from bench-scale testing through implementation. In addition, common failures will be discussed including information on how they may be avoided. Finally, suggestions on where to obtain additional information on the applicability, design, and implementation of ISCO and on how to select support services (engineers and vendors) are provided. It should be noted that due to the sensitivity of ISCO costs and application success to the contaminant mass requiring treatment, an appropriate effort (e.g., direct push mapping techniques) in delineating - and quantifying the target treatment volume and mass are recommended.

ISCO Technology Selection and Optimization

ISCO technologies include CHP, permanganate, ozone and persulfate. It is also common to consider a combination of these ISCO technologies in a single application in a target area or separate applications in different areas of a site to take advantage of the strengths of individual technology (e.g., CHP and persulfate).

Four basic steps are recommended for a project involving ISCO after the initial site screening and an appropriate site assessment:

1. Selection of appropriate technology;
2. Bench-scale tests;
3. Field-scale demonstration (pilot test) if warranted; and,
4. Full-scale application.

The steps presented above represent a pathway that will allow for the appropriate assessment of each technology and the optimization of that technology for each site in a manner that limits the financial risk associated with applying ISCO.

Selection of Appropriate ISCO Technologies

This subsection provides a brief description of each of the common ISCO technologies, including activated persulfate, and the key points with respect to their potential applicability for the treatment of MGP residuals:

- CHP or Fenton’s reagent: Predominantly generates the hydroxyl radical, which is capable of degrading most, if not all, contaminants associated with MGP residuals. CHP is typically the most aggressive ISCO technology but can only be applied to specific sites because of potential issues with subsurface stability of hydrogen peroxide and the evolution of heat and gases. CHP is best suited for conductive soils such as sands or silty sands. If the stability of hydrogen peroxide is not a limiting factor, CHP tends to be the most cost-effective ISCO technology, especially for highly contaminated sites (as is common with MGP sites);

- Activated Sodium Persulfate (e.g., Klozür™): Primary activation mechanisms include iron-chelate, heat, and alkaline activation. Activated persulfate primarily generates the sulfate radical (generation of additional radicals, including the hydroxyl radical, has been measured under the different activation mechanisms) which makes it capable of degrading most, if not all, contaminants associated with MGP residuals. Activated persulfate is generally considered much more stable than catalyzed hydrogen peroxide, resulting in little evolution of heat or gases, which allows for subsurface transport of the oxidant and provides less potential for health and safety issues. The benefit of using activated persulfate is its stability.;
- Permanganate: Effective in degrading a limited suite of compounds, such as chlorinated ethylenes and a number of PAHs, permanganate is not effective in treating BTEX and therefore, is not typically considered for sites impacted with MGP residuals; and,
- Ozone: Under alkaline and neutral pH conditions, ozone generates the hydroxyl radical, which is capable of degrading most, if not all, contaminants of concern associated with MGP residuals. Concerns about the stability and transport of ozone in the subsurface, in the distribution of ozone as a gas in the saturated zone via sparging (limited by relatively minor soil heterogeneities), and on the ozone generation costs for heavily impacted soils may limit the application of this technology at many sites. However, due to its gaseous properties, ozone is well suited for treatment of MGP impacts in the unsaturated zone.

As catalyzed hydrogen peroxide and activated persulfate are seen as the primary ISCO technologies appropriate for most sites containing MGP residuals, a comparison of these technologies is presented in Table 6-2.

Table 6-2
Technology Selection Guidance: Comments on the Selection of Catalyzed Hydrogen Peroxide vs. Activated Persulfate for ISCO at MGP Sites

Category	Characteristics	XDD Generalized Comments[1]	
		Catalyzed Hydrogen Peroxide	**Activated Persulfate**
Soil	Type	Best suited for silty sands, sands and gravels. Ability to treat silts and clays should be tested before application.	Best suited for silty sands, sands and gravels. Better suited than hydrogen peroxide for the treatment of silts and clays, but effectiveness should still be evaluated.
	Hydraulic Conductivity	Better suited for more highly conductive soils.	Stability lends itself to a wider range of conductivities.
	Non-Target Oxidant Demand	Typically minimal impact by non-target demands from soils in comparison to other technologies.	Can be impacted by non-target demand for the oxidant by soils. Non-target demand should be evaluated.
	Geochemistry	Reactivity with site soils can limit application of hydrogen peroxide.	Reactivity with site soils is important, but not as important as with hydrogen peroxide.
Ground water	Flow	High activity and aggressiveness makes hydrogen peroxide better suited for high groundwater flow conditions than persulfate.	Better suited for normal or slower ground water flowrate conditions unless continuous injection methods are used.
Contaminants	Type	Reactive with most MGP residuals.	Reactive with most MGP residuals when activated correctly.
	Mass	Can be effective for a wide range of contaminant mass loadings. Lower oxidant cost favors higher contaminant mass situations.	Can be effective for a wide range of contaminant mass loadings. Persulfate tends to be more expensive than hydrogen peroxide, if applicable.
	Phase	Effective for a wide range of contaminant phases. Research (Smith et al, 2006) indicates may not be dissolution limited, and thus, more effective with DNAPLs.	Effective for a wide range of contaminant phases. May require extended contact time for DNAPL phase contamination.
Site Limitations	Visibility	Can result in evolution of gas and heat which can lead to above ground displays if not designed properly or applied in shallow areas.	Little visible impacts except for injection apparatus.
	Access	Typically lower radius of influence makes application of hydrogen peroxide less favorable in access limited sites.	Typically greater radius of influence makes application of persulfate more favorable in access limited sites.
	Structures	Evolution of gas and heat make hydrogen peroxide less favorable for application beneath buildings unless each can dissipate at rates greater than they accumulate.	Oxidant stability and minimal generation of heat and gases makes the application of persulfate more favorable underneath buildings and other structures.
Oxidant	End Products	Hydrogen peroxide decomposes to form the end products of oxygen and water.	Persulfate decomposes to the end product of sulfate. Sulfate does have a secondary MCL and may not be appropriate for all sites.
	Density	Hydrogen peroxide can be injected at a range of concentrations, but 1 percent to 15 percent is common which would correspond to a specific gravity of ~1.0 to ~1.06. This will result in minimal density driven vertical migration.	Persulfate can be applied at a variety of concentrations and is typically applied from 5 g/L up to 200 g/L. These result in considerable specific gravity range from ~1.05 to ~1.2, which can result in significant downward migration.
	Cost	Typically has the lowest oxidant costs. These cost savings can be offset by various issues and should be evaluated with the systems overall appropriateness for the site conditions.	More expensive than hydrogen peroxide, but costs are less impacted by site conditions.

Notes:

[1] Comments are those of XDD in 2006 are generalizations based on previous experience and an understanding of each technology. These comments will not be applicable to every site. Also, ISCO technologies are expected to continue to evolve as will XDD's concept and understanding on how and when each technology should be applied.

Bench-Scale Tests

Bench-scale tests can be used to determine the appropriate ISCO technology to apply at a site, to identify any potential issues that are not apparent from the typical site investigation data available and to develop the data to assist in the design and optimization of the field-scale application. The primary objective of running bench-scale tests is to identify problems and solutions early in a project so as to avoid costly mistakes. Each ISCO technology has its own set of tests that are recommended to optimize their performance. These tests are often not only specific to the technology and site, but also often specific to each activator mechanism, and even each vendor. The scope of the bench-scale test can be tailored to address site-specific concerns. In general, a typical bench test will evaluate the following:

- Ability of proposed technology to degrade target contaminants to target levels in the presence of site soils;
- Persistence of reagents in the subsurface;
- Potential for interferences and non-target oxidant demands caused by the site-specific soil and groundwater matrix; and,
- Negative impacts caused by reagent addition at the site, such as evolution of heat and gas, or potential corrosion of a structure in the target area.

The bench-scale tests performed for this demonstration, as outlined in Section 4, proved to be critical for the successful implementation of the field demonstration and provide a good example of the importance of bench-scale testing. In the original set of tests for the Laurel Street site, it was observed that the iron-chelate activator did not successfully activate all of the persulfate as some component of the Laurel Street site soils, which could not be definitively identified within the scope of this project, interfered with the iron-chelate activator mechanism. Thus, based on the bench-scale tests, the activator mechanism was switched to alkaline persulfate, which was demonstrated to be effective for the Laurel Street site soils. Further, the tests identified the extraordinarily high non-target demand of the soils and provided an appropriate expectation as to the achievable endpoint/remedial goal for the field demonstration.

Bench-scale tests are usually conducted by analytical laboratories, ISCO engineering firms, or ISCO vendors, and are usually designed by ISCO engineering firms. As a bench-scale test can be critical to the successful implementation, it is recommended that a bench-scale test be designed and completed by capable individuals (discussed below).

Field-Scale Demonstration (Pilot Test)

Field-scale demonstrations, or pilot tests, are usually intended to build on the results of the bench-scale testing by verifying the effectiveness of the treatment technology on a small portion of the site in order to:

- Help identify implementation-related issues that are not typically determined from the bench-scale testing (e.g., hydrogeological conditions); and,
- Validate or refine cost estimates to apply the technology at the full-scale.

As with any *in situ* technology, the primary implementation issue is to verify that contact can be established between the reagents and the contaminant, and therefore the field demonstration is an important element to provide confidence in the potential for the success of the ISCO project. The results of the field-scale demonstration can then be used to make any necessary corrections to the remedial design/approach prior to the application of the technology over the entire target treatment volume.

The size of the pilot test is usually related to the size of the overall project. Small projects typically require a minimal pilot test to evaluate a limited parameter list, such as reagent injection rates and possibly reagent distribution. Larger pilot tests include evaluation of injection rates, reagent distribution, impact of the treatment, and a variety of engineering parameters. These larger field demonstrations are typically designed to remediate the treatment volume as one module of a full-scale treatment application. Some pilot tests are used to also evaluate or verify the applicability of different ISCO technologies based on a side-by-side comparison.

Full-Scale Application of ISCO

Assuming successful bench-scale testing and field-scale demonstration, most projects proceed to the full-scale, and apply the technology (or a combination of technologies) to the entire target treatment volume. Most aspects of a full-scale application are site-specific and, therefore, beyond the scope of the guidance principles presented herein.

In general, full-scale applications are performed in a phased approach, which consists of a baseline monitoring event, the first field application of the ISCO reagents, and a post-application monitoring event. This process allows for additional assessment of the technology and implementation approach, and can help in refining the design of follow-up reagent applications, if needed.

Due to potential health and safety issues and the required quality control, the importance of qualified field crews should not be underestimated. The application may require specific permits or notification of when stored and used on-site.

Common ISCO Failures

Today, successful ISCO projects are commonplace and as the industry's experience continue to grow, failures should become less frequent; however, it is still possible to have a "failed" ISCO application. Besides obvious failures as a result of lack of experience or expertise in the application of the technologies, most other ISCO failures can be generally categorized as a site assessment failure, a technical failure, or a failure to establish realistic remedial goals (based on the site characteristics, bench-scale testing results, etc.).

Site Assessment

ISCO is more dependent upon a site assessment than many other *in situ* remedial technologies. The data generated in a good site assessment should be specific to the area targeted for application, not generalized from a larger non-target area, and should include such parameters as hydraulic conductivity, mineralogy (although the effects of mineralogy may be more cost-effectively determined during the bench-scale testing), contaminant mass, contaminant phase (including general NAPL layer thicknesses), and the vertical and horizontal delineation of the

ISCO target zone. Errors in the determination of these parameters can greatly impact the success and costs of the ISCO application. Some common errors and their resulting impacts include:

- Contaminant mass: Contaminant mass underestimation would result in the under-dosing of oxidant for the site, and consequently the mass reduction goal would not be met, and groundwater concentrations would "rebound" after the application;
- NAPL lenses: Knowledge of the presence and thickness of NAPL lenses is important to ensure that the ISCO application is designed appropriately to meet the remedial goal(s);
- Target soil volume delineation: The cost of ISCO is very sensitive to the target soil volume. An incomplete delineation of a site can both lead to the non-treatment of non-delineated areas that require treatment and/or the extra cost of treating "clean" areas; and,
- Soil heterogeneity: Soil heterogeneity should be understood and incorporated during designing ISCO application parameters including well design, technology selection and expected performance of the application. Brief modeling efforts are relatively inexpensive to perform, and are often beneficial in evaluating the potential impacts of the soil heterogeneity during the ISCO application design.

Technical Considerations

Technical failures are often the result of improper design or failure to test for the parameters sensitive to the success of each ISCO technology under consideration. Areas of concern to closely monitor and potential impacts include:

- Well placement/radius of influence:
  - The larger the area a well is intended to cover (e.g., radius of influence) the greater the chances of incomplete reagent distribution (this parameter is especially sensitive to heterogeneity effects);
- Pore volume:
  - Injecting less than a complete pore volume during an injection event may require using more reagents to treat the entire target soil volume. At some sites this approach may be adequate to meet the remedial goals; however, by injecting a full pore volume within an application, the probability of contacting the reagent with the contaminant over the entire radius of influence of the injection point is higher;
- Vertical screen placement:
  - The vertical interval of the sand pack (where sand packs are used) around the screen is most likely what will dictate the vertical interval that will be treated by the reagents. The larger the vertical interval, the more likely that preferential flow of the reagent and incomplete contact with the target soil volume will occur. Also, it is important to make sure that the entire vertical interval of the sand pack will receive effective treatment (density effects of the injected reagents does require consideration, primarily in soils with a low vertical to horizontal conductivity ratio);

- Injection rate:
  - The injection rate directly controls how long it will be necessary to be on site to deliver the design injection volume of reagents. Too low of an injection rate can require significant time on site and therefore increase project costs. A high injection rate/pressure can lead to the formation of preferential flow paths in the subsurface and may also result in “day lighting” of the reagents at the surface; and,
- Technology specifications:
  - An assessment of all site impacts on a technology, including geochemistry, mineralogy, etc. is advised. The advantages and disadvantages of the two primary applicable oxidants for MGP sites are presented in Table 6.2.

Remedial Goals

As discussed throughout this report, appropriate endpoint expectations or remedial goals for the application of ISCO at a site are as important to the success of a project as any technical aspects of the project. When developing the remedial goals for an ISCO project, it must be recognized that ISCO is a mass reduction technology where performance is best evaluated through composite soil sampling. The beginning of this section details applicable site selection criteria and expectations for remedial goals for ISCO applications at MGP sites.

ISCO Support Services (Engineer and Vendor Selection)

It is important to note that ISCO technologies are still evolving and are complex relative to most other *in situ* remedies. ISCO technologies involve numerous chemical reactions between reagents, soils and the target contaminants, and the reagents themselves can be hazardous if not handled properly. It is not an “off the shelf” or “one size fits all” technology, and there are several potential technical issues that must be evaluated throughout the phases of a project, from the preliminary screening through the design, testing, and implementation phases. Also while implementation has occurred over the last 15 years the level of expertise and experience in the industry continues to evolve. Because of these factors, a key to the successful implementation of an ISCO project today includes the selection of a capable ISCO engineering firm and/or vendor.

Site managers should take the following recommendations into consideration:

- Obtain qualification information from a vendor’s previous projects;
- Obtain and check references for previous ISCO work and ISCO expertise and publications;
- Consult with federal agency ISCO specialists. The US EPA, United States Army Corps of Engineers and several other agencies have internal personnel to aide project managers;
- Request direction and/or information from one or more of the several university professors that have programs studying the mechanisms involved in ISCO;
- Attend and/or obtain information from the several conferences and workshops that dedicate sessions to ISCO where companies and researchers often present their results.
- Consult the peer-reviewed literature.

ISCO Cost Overview

The cost of an ISCO project is similar to most other remedial projects in that the cost tends to increase with increasing area and volume to be treated. Because ISCO is based on the reaction of the reagent with the contaminant, reagent costs are very closely related to the mass of contaminant. ISCO technologies typically are applied at costs ranging from approximately $100 to $500 per cubic yard (in year 2006) with exceptions that are dependent upon the site-specific circumstances. In general, ISCO costs tend to increase with:

- Volume of soil to be treated;
- Contaminant mass;
- Presence of NAPL;
- Non-target demand in soil;
- Level of soil heterogeneity;
- More stringent remedial goals; and,
- Limited or decreasing hydraulic conductivity.

To illustrate what a site manager may expect for relative costs to apply ISCO using activated persulfate or catalyzed hydrogen peroxide at an MGP site, relative costs for four site scenarios are presented in Figures 6.1, 6.2, 6.3 and 6.4 to represent the factors that tend to dictate remediation costs: varied degree of COC impact (target contaminant mass), hydraulic conductivity, site size, and remedial goals. The relative costs are meant to provide the site manager with the major components that should be considered in estimating remedial costs using ISCO. It is important to note that catalyzed hydrogen peroxide is often less expensive than activated persulfate to apply at similar sites. However, catalyzed hydrogen peroxide is also significantly more sensitive to site conditions and ultimately cannot be applied in all instances. This is discussed in more detail in Table 6.2.

MGP Residual Scenario 1: Varied Degree of Contaminant Impact

Scenario 1 is intended to illustrate the impact of increasing contaminant mass on the cost of applying ISCO. Ultimately, the phase of contamination is often linked to the mass, with increasing concentrations of contaminant indicative of sorbed, residual and NAPL phase contamination. The scenario assumes a remedial goal of TPH reduction of 500 mg/Kg, 1,000 mg/Kg, and 10,000 mg/Kg. It is assumed that the site has adequate hydraulic conductivity to receive the reagents at 5 gallons per minute (gpm) per injection point.

The relative cost evaluation chart (Figure 6-1) indicates that while cost per cubic yard increases with increasing target contaminant mass, the cost per pound of contaminant degraded significantly decreases. This is a function of the fact that reagent costs and the mass of contaminant degraded are variables in this scenario, but the target volume remained the same. It should also be noted that activated persulfate was more cost-effective at sites with lower concentrations, which is due to lower well installation and application costs.

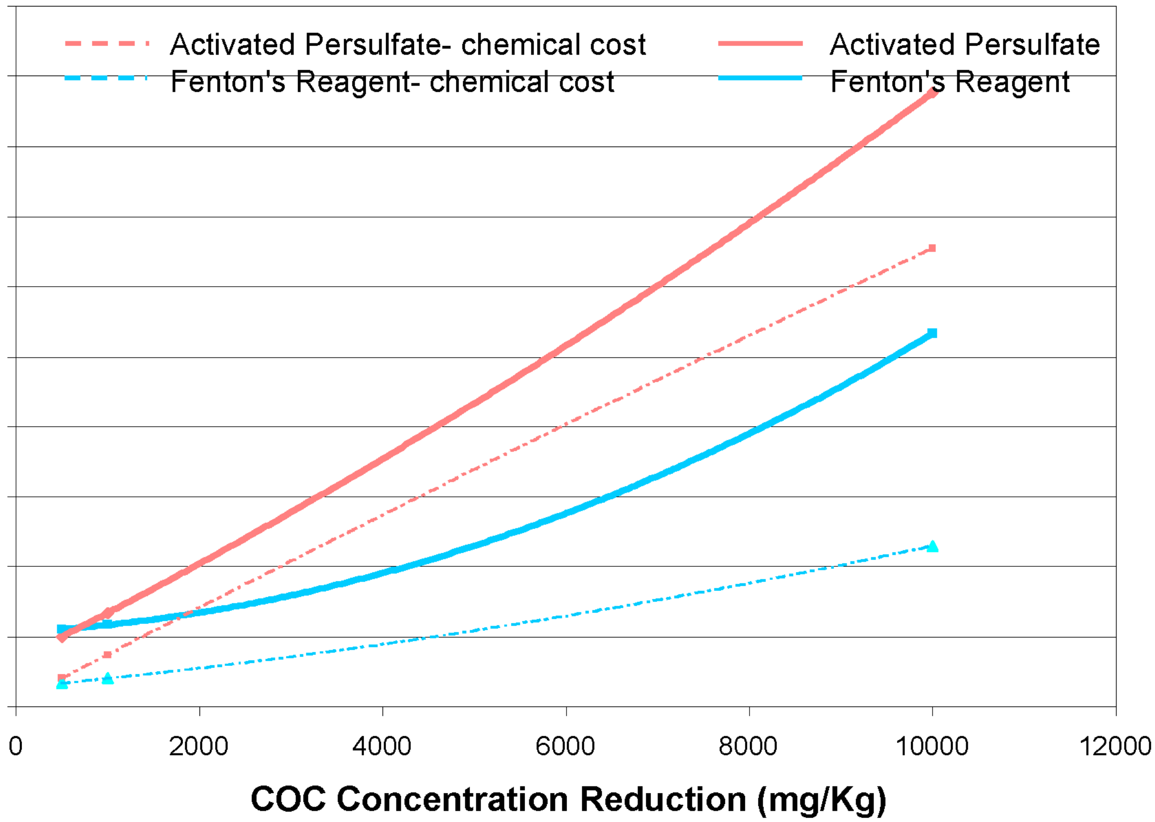


Figure 6-1
ISCO Cost Guidance: Scenario 1

MGP Residual Scenario 2: Varied Hydraulic Conductivity/Rate of Injection

A common limitation during the application of ISCO technologies is the rate at which the ISCO reagents can be injected, which is a result of the site's hydraulic conductivity. Scenario 2 presents the impact of injecting at flow rates of 0.2 gpm, 1 gpm, and 5 gpm per injection point.

The relative cost evaluation chart (Figure 6-2) shows that as the injection rates decrease, the cost of the application rapidly increases. This is simply due to injection time required to get the necessary volume of reagent into the subsurface. Activated persulfate, in this scenario, is favored at the lower flow rates while catalyzed hydrogen peroxide is more cost-effective at the higher flow rates. Their costs are similar at a flow rate of 1 gpm.

MGP Residual Scenario 3: Site Size

Scenario 3 iss intended to illustrate the differences in costs that can occur as the size of a site, and associated soil volume to be treated, is varied. In this scenario, areas of 500, 5,000, and 50,000-square feet were considered. The soil is relatively homogeneous fine sands with silts, with the ability to receive 5 gpm of reagents per well continuously. Figure 6-3 presents a relative cost evaluation chart.

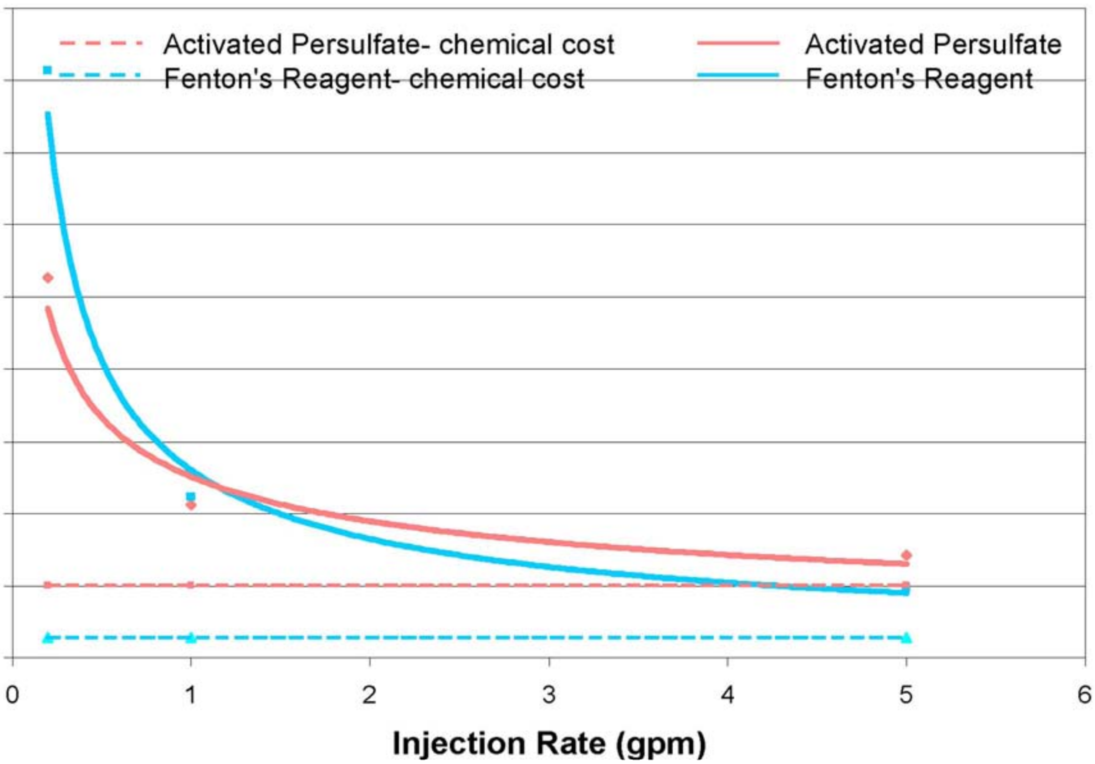


Figure 6-2
ISCO Cost Guidance: Scenario 2

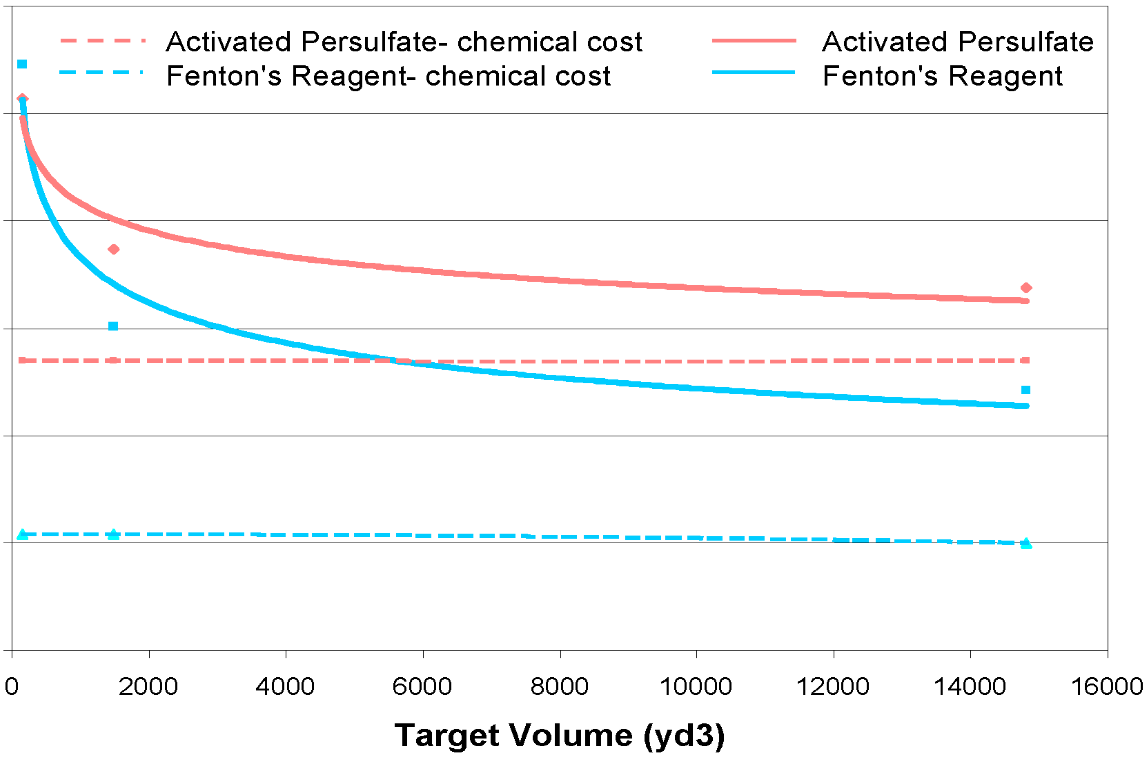


Figure 6-3
ISCO Cost Guidance: Scenario 3

The relative cost per cubic yard and cost per pound of contaminant-degraded decrease with increasing site size. This is a result of various economies of scale associated with larger sites. It is also important to note that catalyzed hydrogen peroxide may be more cost effective for medium and larger sites while activated persulfate may be more cost-effective for smaller sites.

MGP Residual Scenario 4: Varied Remedial Goals

Often the same amount of mass can be removed, but the relative cost of the project will vary because the target percent of mass reduction is different as a result of remedial goals. Scenario 4 evaluated the hypothetical relative costs associated with degrading the equivalent of 5,000 mg/Kg TPH at three sites with different starting soil concentrations: 1) 15,000 mg/Kg TPH to 10,000 mg/Kg, for a 33 percent reduction in total mass; 2) 5,500 mg/Kg TPH to 500 mg/Kg, for a 90 percent reduction in total mass; and 3) 5,005 mg/Kg TPH to 5 mg/Kg, for a 99 percent reduction in total mass.

Figure 6-4 shows that relative costs increases as percent mass reduction increases despite the fact that the same amount of COC mass is being degraded. This is a result of assumptions made that the ISCO technologies have slightly lower efficiencies in degrading higher percentages of oxidant. These assumptions are based on XDD’s observations and experience, as well as the general theory, that the initial portions of contamination are more readily available and that the lowest concentrations of contamination tend to be the least available to oxidize.

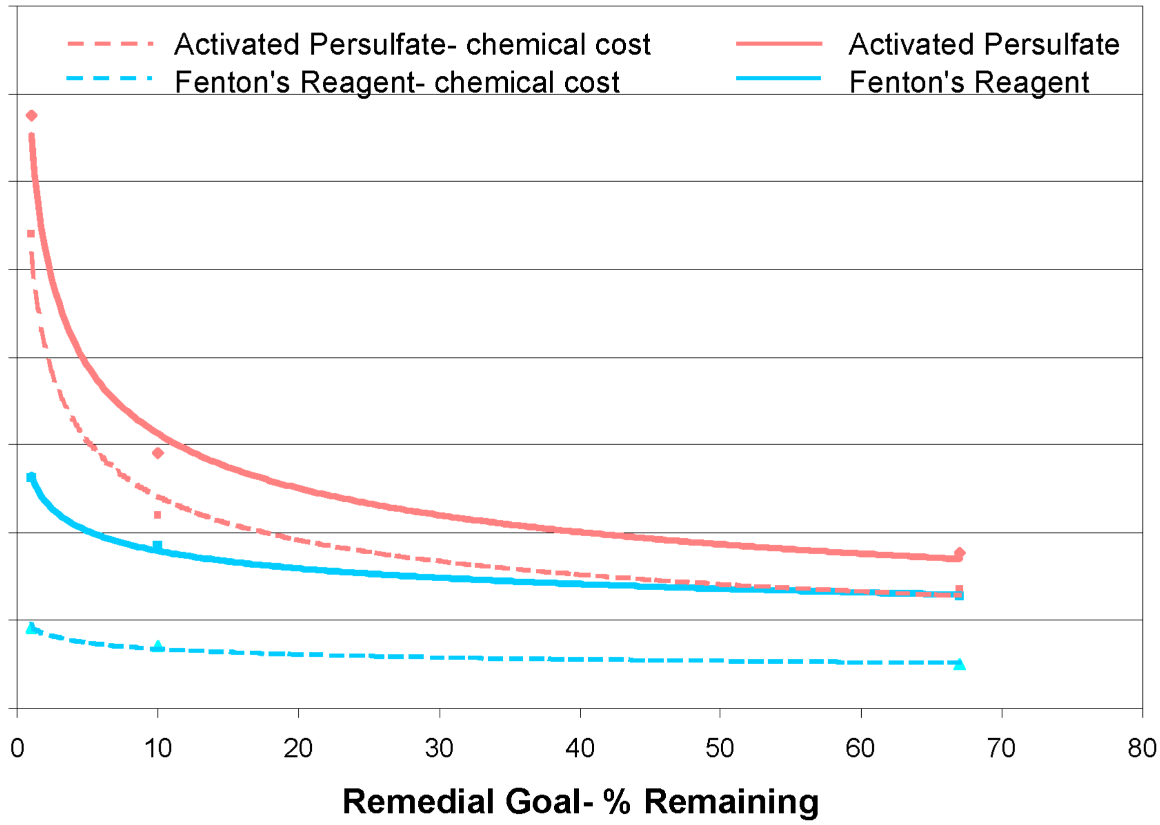


Figure 6-4
ISCO Cost Guidance: Scenario 4

ISCO Cost Summary

Overall, for the scenarios evaluated, catalyzed hydrogen peroxide tends to be less expensive in more instances than activated persulfate, with activated persulfate tending to be favored at smaller, less contaminated or at sites with lower hydraulic conductivity or site access limitations. It is important to note that the results may vary with different base assumptions, and that although catalyzed hydrogen peroxide is estimated to be less expensive than activated persulfate, it can only be applied to a limited number of sites because of site-specific conditions discussed earlier in this section. Conversely, where it can be applied, catalyzed hydrogen peroxide may typically be less expensive at sites with the high mass loadings typical of MGP sites.

7

CONCLUSIONS

ISCO is a technically complex yet promising technology that can treat a wide range of contaminants including constituents found in MGP residuals. It is an *in situ* technology that proves to be a cost-effective alternative, especially for areas that are inaccessible or too deep to consider excavation and treatment off-site. ISCO reactions occur relatively rapidly, on the order of hours to months. While there are potential benefits associated with ISCO, it should not be considered a universal remedy for every MGP site.

Section 6 provides a detailed discussion and general guidance principals on screening of sites to evaluate if ISCO may be a cost-effective remedial alternative and general ISCO application guidance including endpoint expectations and potential failure mechanisms. The following is a list of conclusions made based on this ISCO demonstration work.

- Bench scale testing provided critical information for the design and success of the field demonstration that is generally not collected during site investigation work. The bench tests demonstrated both the importance of the soil properties on the applicability of ISCO and the flexibility of activated persulfate to degrade MGP residuals under a variety of soil conditions.
- The collective results of the bench-scale tests conducted on soils from the two MGP sites (North Water Street and Laurel Street sites) showed that iron-chelate-activated persulfate was effective in treating soils from the North Water Street site, and that alkaline-activated persulfate was effective in treating soils from the Laurel Street site. Greater than 90 percent reductions in MGP constituents (e.g., PAHs and TPH) and TOC concentrations were observed due to oxidation by activated persulfate.
- Due to the atypically high COD in the Laurel Street site soils and bench testing results, the objective and scope of the field demonstration were adjusted to achieve approximately 50% mass reduction of PAHs and TPH by a single application of alkaline-activated persulfate.
- The field demonstration met the project objectives including the evaluation of technical feasibility, economics and limitations of applying ISCO for MGP residuals using activated persulfate.
- The field demonstration performance monitoring data gathered at the time of the ISCO application indicates that the influence of the alkaline persulfate application extended well beyond the targeted treatment area.
- Activated persulfate degraded the wide suite of constituents found within MGP residuals. As expected based on the bench-scale test results, the single field application of activated persulfate destroyed the PAHs and TPH by approximately 40 to 60 percent. Based on the bench testing results, greater than 90 percent reductions in PAHs and TPH may be achieved with additional activated persulfate applications.

- Accurate estimation of the transferable oxidant loading criteria based on this demonstration was hindered by the measured oxidant influence outside the target area. However, based on the calculated contaminant mass reduction and known mass of persulfate application, the oxidant loading rate was calculated to be approximately 14 to 38 pounds of sodium persulfate per pound of TPH degradation, and approximately 59 to 153 pounds of sodium persulfate per pound of PAHs degradation.
- The BTEX mass in the target area appeared to be unchanged after one field application. This result is counter to what would be expected, and is believed to be due to the availability of the BTEX for oxidation in the site soils. It is hypothesized that the BTEX may be tied up in the less readily available organics, and that any BTEX in the readily oxidizable organics was likely flushed or degraded from the area prior to the demonstration.
- Activated persulfate application reduced contaminant mass flux in groundwater at MGP sites. The single application of activated persulfate reduced the leachability of PAHs and BTEX compounds by 63 and 26 percent, respectively. Further reduction in contaminant leachability may be achieved by additional activated persulfate applications.
- NAPL mobilization and accumulation was not observed during the activated persulfate field application at the Laurel Street site, however, NAPL mobilization of short distances is a possibility, and should be monitored during ISCO applications.
- With appropriate engineering and health and safety measures, activated persulfate was applied safely during the field demonstration. No significant heat or gas evolution was observed during the field application.

8
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