

FINAL REPORT
PHASE ONE FIELD DEMONSTRATION OF
***IN SITU* BIOGEOCHEMICAL STABILIZATION**
(ISBS) FOR CREOSOTE/PENTA RESIDUALS
(NAPL)

KOPPERS, INC.
DENVER, COLORADO

Prepared for

Beazer East, Inc.
PITTSBURGH, PA

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PHASE ONE FIELD DEMONSTRATION OF *IN SITU* BIOGEOCHEMICAL STABILIZATION (ISBS) FOR CREOSOTE/PENTA RESIDUALS (NAPL)

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1.0 EXECUTIVE SUMMARY

Beazer East, Inc. (Beazer) developed a Long-Term Interim Corrective Measures Compliance and Performance Monitoring Plan (GeoTrans, Inc., May 4, 2001) for the various interim measures (IM) groundwater remedies at the Koppers Inc. Site in Denver, Colorado (KI Site). As described in the Corrective Measures Study Report dated July 2, 2001 (GeoTrans, July 2001), the IM ground water remedies were supplemented with the following technologies to enhance the removal of constituents of interest (COI) present in groundwater located off-property:

- i. Remediation by (monitored) natural attenuation (RNA);
- ii. Phytoremediation; and
- iii. *In situ* biogeochemical stabilization (ISBS) of creosote residuals.

This report describes the results of the initial (Phase I) engineering optimization field tests where 24,050 gallons of 3% aqueous permanganate (KMnO₄) solution was injected into 13 locations within a defined test area (75 x 95 ft). Performance monitoring was conducted for 5 months to evaluate the ability ISBS using KMnO₄ to stabilize the suspected free-phase non-aqueous phase liquid (NAPL) residuals and enhance the natural attenuation processes by:

- i. Mitigating the migration of NAPL;
- ii. Reducing the concentration of COI in the dissolved-phase;
- iii. Decreasing the mass of NAPL residuals (source reduction); and
- iv. Reducing the flux of COI from NAPL residuals (especially true with MnO₂ precipitate).

As documented herein, the ISBS approach appeared to mitigate the migration of NAPL within the initial test area. As such, ISBS represents a useful tool for *in situ* NAPL management. Information from the Phase I effort described herein has been used to modify the approach for possible continued, larger-scale implementation of the ISBS technology as a supplemental means of source area / NAPL management at the KI Denver Site.

2.0 INTRODUCTION

Over 70 years of wood-treating operations at the KI Denver Site has resulted in creosote/penta non-aqueous phase liquids infiltrating to the shallow ground water beneath the Site. The on-property dissolved-phase COI plumes are present in the alluvial (A-zone) and bedrock deposits (B-, C-, and D-zones). Conversely, the off-property dissolved-phase COI plumes are primarily restricted to the A- and B-zone deposits. The dissolved phase ground water in this formation contains pentachlorophenol (penta) (**Figure 1**) and the lower-molecular weight polycyclic aromatic hydrocarbons (PAHs), mainly naphthalene (**Figure 2**). The light non-aqueous phase liquids (LNAPLs) in the A-zone (**Figure 3**) are the primary source of dissolved penta and PAHs in Site ground water. The dense non-aqueous phase liquids (DNAPLs) are a secondary source of COI in the dissolved phase A-zone aquifer (**Figure 4**).

2.1 NAPL Conceptual Model for KI Site

The conceptual model for the presence of NAPLs in the subsurface at the KI site is that NAPLs infiltrated through the base of the unlined lagoons, impoundments and wastewater ditches during the period of 1928 to 1985. The light-phase NAPLs (specific density less than water) floated on top of the water table and the dense-phase NAPLs sank until they encounter the low-permeability weathered bedrock surface. During the approximately 57 years that the lagoons, impoundments and ditches were in use, infiltration of wastewater/NAPLs caused the LNAPLs to migrate towards the northeast, in the direction of groundwater flow. DNAPLs sank to the top of the bedrock surface and slowly migrate along this surface where they pooled in topographic bedrock depressions and/or infiltrated deeper into the bedrock via vertical fractures.

Subsurface movement of DNAPL is controlled substantially by the nature of the release, DNAPL density, interfacial tension, viscosity, porous media capillary properties, and usually to a lesser extent, hydraulic forces (EPA/Cohen and Mercer, 1993). In addition, NAPLs with specific densities close to that of water can potentially change from LNAPLs to DNAPLs with slight variations in temperature. Laboratory tests that evaluated the subsurface migration of DNAPLs were conducted by Schuille (1988). In cases where sufficient DNAPL reaches the water table, the denser liquid moves downward to the base of the aquifer, locally accumulating on low-permeability horizons within the aquifer. NAPLs will continue to migrate in the subsurface until they either become trapped or the NAPL is distributed along the transport pathway at residual saturation and NAPL

migration stops. Data indicate that most NAPL accumulations at the site are at or below residual saturation, and are therefore immobile.

Historically, the surface lagoons, impoundments and wastewater ditches were the primary sources of LNAPLs and DNAPLs at the KI site. The lagoons were closed in 1975 by removing all free liquids, recovering and recycling creosote soils, backfilling the lagoons with soils, and treating any sludges that remained with fertilizers. Two surface impoundments and an unlined ditch were closed in about 1985. Therefore, all known NAPL sources at the KI site have been removed.

IT (1999) estimates that 180,000 gallons of LNAPL and 455,000 gallons of DNAPL are present in subsurface materials at the site; however, only a small fraction of this NAPL is potentially recoverable. Numerous laboratory analyses and pilot tests of NAPL recovery have been performed at the KI site since 1994. The results of laboratory analysis support in-situ pilot tests that demonstrate significant LNAPL and DNAPL recovery is technically impracticable at the site.

2.2 On-Property Interim Measures Ground Water Remedy

An IM on-property groundwater remediation system was constructed at the KI site to mitigate the off-site migration of impacted groundwater and LNAPLs (GeoTrans May 4, 2001). The IM groundwater remedy consists of several integrated components: i) a physical barrier wall, ii) an *in situ* aerobic treatment curtain (ATC) and, iii) an anaerobic treatment zone (ATZ) (**Figure 5**). The physical barrier wall consists of 2,400 feet of interlocking steel sheet piles driven through the A-zone into the weathered bedrock. The sheet-pile joints are sealed with a bentonite grout to prevent leakage through the joints. The primary purpose of the physical barrier wall is to mitigate the off-site migration of impacted groundwater from the KI site and redirect the ground water through the *in situ* biological treatment systems.

2.3 Off-Property Ground Water Remedy

In collaboration with the University of Waterloo (UW) Department of Civil Engineering and Earth Sciences, GeoTrans, Inc. and Malcolm Pirnie, Inc. (formerly with URS Corporation), Beazer developed an ISBS Field Activity Plan (FAP) describing the initial pilot-scale field application of ISBS technology for stabilization of off-property creosote/penta organic residuals (*e.g.*, NAPL) at the KI Site in Denver (URS Corporation August 24, 2001). The short-term goal of the ISBS technology was to reduce the free-phase NAPL thickness and recovery volumes in wells within the defined test

area, which measured approximately 75 ft x 95 ft. As described below (Section 3.0), *in situ* NAPL stabilization is caused by a combination of *weathering*, chemical oxidation and physical encrustation of the organic residuals with precipitated manganese dioxide (MacKinnon and Thomson, 2001). The significance of this initial stabilization affect was determined by physically monitoring reduced accumulation of NAPL within a series of wells. The longer-term goal of ISBS is to reduce the flux of COI from the residual NAPL sources into the dissolved phase, thereby enhancing the affects of RNA to reduce the size and magnitude of the off-property dissolved-phase COI plume. The ability of the ISBS approach to enhance RNA processes was not assessed during the current study.

2.4 Objectives of the ISBS Field Validation Efforts

The objectives of these initial field efforts were to:

- i. Evaluate the ability of the ISBS processes to stabilize creosote/penta NAPL residuals at the KI Site;
- ii. Collect ISBS performance monitoring data that are complementary to those obtained through the related efforts of the Long-Term Interim Corrective Measures Compliance and Performance Monitoring Plan Program and RCRA Permit Compliance Monitoring Plans; and
- iii. Obtain data useful for optimizing the implementation of larger-scale technology application.

3.0 ISBS FOR SOURCE AREA STABILIZATION

In situ biogeochemical oxidation for the purposes of NAPL stabilization entails the use of a chemical oxidizer, such as Fenton's Reagent (H_2O_2 , Fe^{2+}), persulfate with ferrous ions, peroxymonosulfate, KMnO_4 , or sodium permanganate (NaMnO_4) that is flushed through an aquifer zone suspected to contain residuals NAPL. As the oxidant migrates through the targeted source area, the various (bio)geochemical reactions that occur between the organic COI and the oxidant cause the destruction or removal of NAPL via a two step process; i) oxidation, and ii) dissolution. The chemical/biological oxidation processes destroy COI present in the dissolved phase. This, in turn, increases the release of COI from NAPLs into the aqueous phase. In theory, the more water soluble, lower-molecular-weight creosote constituents will be dissolved and treated/removed at a proportionally higher rate, thus leading to a "hardening" or chemical "weathering" of the NAPL as it steadily loses its more labile components. This causes a net increase in viscosity of the organic material, which yields a more stable, recalcitrant residual mass. As such, the flux of COI released into the dissolved phase is much reduced and natural attenuation processes are more easily capable of managing associated plumes (MacKinnon and Thomson, 2002).

3.1 Stabilization via Physical Encrustation

At a pH range of 3 to 11, KMnO_4 oxidation reactions proceed via a three-electron transfer resulting in the formation of manganese dioxide (Equation 1):



The MnO_2 precipitate that results from permanganate oxidation reactions is insoluble, has high surface area, is a good coagulant, and has high sorptive capacity for divalent cations (Pisarczyk and Rossi, 1996). Conventionally, this is often considered problematic because of the potential for the MnO_2 to cause chemical fouling and reduction in aquifer permeability (Yin and Allen, 1999). However, when the technology is viewed as described herein (*i.e.*, as *in situ* source stabilization), then this precipitation or encrustation affect is actually desired.

In the presence of an organic compound (R), reaction of permanganate produces manganese dioxide (as described above) and either carbon dioxide or intermediate oxidized organic compounds (R_{ox}) as summarized below (Equation 2):



The additional benefit of using KMnO_4 as the oxidizing agent is that MnO_2 will precipitate along the NAPL interface thereby reducing the flux of dissolved-phase constituents into groundwater. Separate laboratory studies conducted by Dr. Neil Thomson of the UW documented this effect (See inset 6.1).

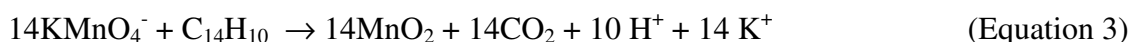
Inset 6.1. Sections of a sand (white) NAPL (red) interface treated with KMnO_4 (dark purple/brown) and encrusted with precipitated MnO_2 (Black).



Photo Courtesy of Dr. Neil Thomson, University of Waterloo.

3.2 Stabilization via Oxidation and Dissolution

The following example (Equation 3) represents a typical reaction between a non-halogenated PAH (*i.e.*, phenanthrene; $\text{C}_{14}\text{H}_{10}$) and KMnO_4 where the organic compound is mineralized completely to CO_2 :



Phenanthrene is often used as a model PAH in a creosote mixture. Stoichiometrically, Equation 3 suggests that 14 moles of either potassium or sodium permanganate are required to completely oxidize/mineralize this compound. In the process, 14 moles of MnO_2 are deposited *in situ*. This assumes, however, that there are no additional oxygen sinks. Since inorganic oxygen demand is likely to be present, more KMnO_4 would, in theory, be required to mineralize the carbon *in situ*. However, the objective of source stabilization via ISCO is flux reduction via weathering and encrustation as opposed to complete mineralization of all resident PAH. Source stabilization can be attained with approximately 65-percent less permanganate than would be required for complete mineralization (see below).

3.3 UW Research on MnO₄ for Stabilization of Creosote Residuals

The chemical oxidation process enhances the removal of creosote NAPL by: a) increasing the mass transfer zone by decreasing concentration of creosote compounds in the aqueous phase, b) increasing the aqueous solubility of less readily oxidizable compounds by increasing their mole fraction, and c) increasing the mass transfer process through the diffusion of permanganate into areas of low permeability. Specifically, for the more readily oxidizable, water-soluble, or otherwise “labile” compounds such as naphthalene, the rate of oxidation is greater than the rate of dissolution. For the less readily oxidizable compounds, such as chrysene, the rate of oxidation was slow compared to the rate of dissolution. The aqueous concentrations for these compounds were not reduced. However, a significant increase in the rate of removal of these compounds was observed compared to a column without oxidation. This is due to the rapid removal of the more readily oxidizable compounds from the NAPL, which increased the mole fraction of the less readily oxidizable compounds. Thus according to Raoult’s Law the concentration in the aqueous phase becomes closer to its pure phase liquid solubility and its aqueous concentration increases. Since their aqueous concentrations are increased more mass is removed from the oil phase.

Results of laboratory experiments conducted at UW showed that there was indeed an unequal or disproportional enhancement in the dissolution process. At 8 % residual creosote saturation in soil, individual creosote constituents exhibited a wide range of reactivity towards permanganate and therefore the extent of oxidation at the oil/water interface was different for each compound. Specifically, the most significant removal occurred with readily oxidizable compounds having lower molecular weight, such as naphthalene, pyrene, and fluorene (see Inset 3.1). Compounds that have low aqueous solubilities such as chrysene are not readily oxidizable and may require a long period of time to be removed, but the interval is greatly reduced compared to flushing the area with water alone.

Inset 3.1. Comparison between no oxidation, oxidation and flow rate. The time and pore volumes needed to reduce the mass of the creosote compounds by 1/100.

Courtesy of Dr. Steve Forsey, University of Waterloo.

Linear Velocity (m/s)	4.97x10 ⁻⁶		4.97x10 ⁻⁶		4.97x10 ⁻⁵	
[KMnO ₄] (g/L)	0.0		15.0		15.0	
	Days	Pore	Days	Pore	Days	Pore
Compounds		Volumes		Volumes		Volumes
Naphthalene	58.0	215.1	8.5	31.5	4.5	165.8
1-methylnaphthalene	237.0	878.8	16.0	59.3	11.0	405.4
Biphenyl**	298.0	1104.9	53.5	198.4	17.0	626.5
Acenaphthene	1359.0	5039.0	13.5	50.1	11.5	423.8
Dibenzofuran**	1384.0	5131.7	53.0	196.5	16.0	589.7
Fluorene	2684.0	9951.9	14.5	53.8	12.5	460.7
Phenanthrene	4000*	14831.5	32.0	118.7	21.5	792.4
Anthracene	922.0	3418.7	16.0	59.3	13.5	497.5
Carbazole	345.0	1279.2	14.5	53.8	12.0	442.2
Fluoranthene	3895.0	14442.1	36.0	133.5	22.5	829.2
Pyrene	4000*	14831.5	22.0	81.6	17.0	626.5
Chrysene**	4000*	14831.5	257.0	952.9	41.0	1511.0

* Concentration not reduced to 1/100 of its original mass. ** Compounds not readily oxidized.

3.4 Advantages of MnO₄ for Stabilization of Creosote/Penta Residuals

For the purposes of using ISBS for stabilization of organic residuals or NAPL, advantages of using MnO₄ include the following:

1. High concentration of MnO₄ insures that the oxidizing reagent concentration does not become limiting and that the rate of COI oxidation is optimal. High concentrations of MnO₄ can be applied - up to solubility limits of approximately 6% (60 g/L at 68 degrees F, or 20 C) for KMnO₄ or 40% for NaMnO₄. At colder groundwater temperatures of 16 C (60 degrees F) for the KI Denver Site, the solubility of KMnO₄ was estimated between 3 to 4%.
2. Permanganate exhibits fast reaction time (0.5 to 1 month) in the presence of organic material, but non-reacted MnO₄ will persist in the subsurface for several months. As the solution migrates through the aquifer formation, excess MnO₄ allows the oxidation process to take place throughout the targeted area not just near an injection point.
3. Encapsulating of NAPL residual in the targeted zone with MnO₂ may decrease the concentrations of COI leaching from NAPL to very low or negligible concentrations thereby stabilizing the source

area.

4. KMnO_4 is an easily handled free flowing solid available as 99% active ingredient; NaMnO_4 is a liquid commercially available at a 40% solution. Delivery of the material to the subsurface requires standard equipment and routine health and safety operations.

3.5 Disadvantages of MnO_4 for Stabilization of Creosote/Penta Residuals

There are at least four recognized potential disadvantages of using MnO_4 for stabilization of creosote/penta residuals via ISBS:

1. Creosote contains a wide range of organic compounds, many of which are readily biodegradable or otherwise readily oxidized. As these materials are biodegraded, there is a significant reduction in redox and dissolved oxygen yielding reducing conditions in the subsurface. In turn, inorganic alternative electron acceptors such as iron, manganese, nitrate, and sulfate are reduced. The introduction of permanganate or another chemical oxidant provides an alternate oxygen source for the oxidation of reduced organic and inorganic matter. Thus, the amount of reduced iron and other potential oxygen sinks is important in determining the kinetics of oxidant consumption.
2. Perhaps more significant, in cases where NAPL saturations are significantly above the residual saturation, is the potential for physical displacement and subsequent mobilization caused by the introduction of large volumes of material to the formation. To help avoid physical displacement, lower volumes of liquid containing higher concentration of KMnO_4 can be added in a pulse delivery method.
3. A secondary plume of trace metals such as manganese and possibly lead, chromium or arsenic may occur. These plumes can result from the large mass of manganese introduced into the formation; and the trace amounts of arsenic and other metals may be present as impurities.

4.0 MATERIALS AND METHODS

4.1 Phased Field Application of ISBS Reagents

Two areas were chosen for field validation of ISBS using KMnO_4 or possibly a Fenton's-type reagent. As prescribed in the FAP, reagents may be applied in three phases (**Figure 6**):

- Phase I: Initial application of KMnO_4 to a defined testing location in the southernmost off-property NAPL area.
- Phase II: Based on the results from Phase I additional KMnO_4 may be applied to the remaining area of the lower off-property NAPL source.
- Phase III: Based on the results from Phase I and Phase II efforts, permanganate may be applied to the northern off-property NAPL area.

This report presents the results of the Phase I implementation and monitoring.

4.2 Application of KMnO_4 - Phase I

The materials and methods for conducting field-scale optimization tests of the ISBS approach were described in the site-specific Field Activity Plan (URS Corporation August 24, 2001). Critical processes and procedures are summarized below along with descriptions of any deviations from the FAP. The following schedule was realized:

PHASE I	DATE
IM Baseline Monitoring	September, 2001
Engineering and Design Phase	October-November, 2001
Laboratory Engineering Optimization Studies	December, 2001
Injection Piezometer Construction	August, 2002
Permanganate Delivery	September 7-14, 2002
Performance Monitoring	September, 2002 through February, 2003
Post Treatment Soil Coring and Residuals Testing	May, 2003
Draft Report - Phase One	July, 2003
Final Report - Phase One	October, 2003

4.2.1 Laboratory Engineering Optimization Studies

Research conducted by UW using soil samples from the Phase I area of the KI Site concluded that: 1) treatment with KMnO_4 at 15 g/L provided effective NAPL stabilization, and 2) injection of KMnO_4 at high concentrations using low flow rates and a pulse-pumping delivery method enhanced distribution and mixing while minimizing the potential for NAPL displacement. Initial experiments with soil collected from the Phase I area of the KI Site contained approximately 8% creosote (GeoTrans, Inc. January 6, 1999) and exhibited a natural oxidant demand (NOD) of 18 g/kg soil (**Appendix A**). Batch reactor studies, with KI Site soils, demonstrated the enhanced removal of creosote constituents using KMnO_4 at 8 g/L. After 39 pore volumes, the KMnO_4 oxidizing solution decreased the initial mass of creosote compounds by 36.5%, whereas in the control column (no oxidizer) only 3.85% was removed. With a KMnO_4 concentration of 15 g/L, 69% of the 12 monitored creosote compounds were removed after 5 days compared to only 5% removal of the compounds if only water was flushed through the column.

Subsequent column studies using soil from the KI Site demonstrated effective treatment using 25% of the calculated NOD, or 4.5 g KMnO_4 / kg soil (**Appendix B**). At this permanganate concentration, significant creosote removal was observed, and decreases in soil permeability were noted. This combination of affects was demonstrative of the overall concept of NAPL stabilization and reduction in mass flux from the targeted source zone. This was the KMnO_4 concentration used for the Phase I treatment program.

4.2.2 KMnO_4 Injection Points

Seventeen injection points (IP-1 through IP-17) were installed in August 2002 approximately 15-feet apart throughout the Phase I treatment area (**Table 1; Figure 7**). Thirteen of these injection points were used to inject KMnO_4 solution as described below (see Section 4.2.4); the remaining four IPs (IP-04, IP-13, IP-15 and IP-16) were used for performance monitoring (see Section 4.2.3). Each of the IPs were installed with a 4-inch internal diameter hollow-stem auger to a depth from 15.3 to 22.5 ft below ground surface (bgs) to the top of the B-Zone formation (see Figure 5). The IPs were constructed of schedule 40 PVC with five feet of screen (slot size 0.020 inches) surrounded by an appropriately sized coarse sand pack. The screen intervals were positioned to target the saturated alluvial A-zone deposits (Table 1), which averaged about 2-feet thick in the Phase I Area.

4.2.3 Performance Monitoring Wells and Piezometers

Fourteen existing groundwater wells (**Table 2**) and three of the newly installed IPs (IP-13, IP-15 and IP-16) were used to monitor the performance of the Phase I ISBS process. Well IP-04 was used for field monitoring and did not receive permanganate injections. Seven of the monitoring wells (SVW-2, M8A, PT-02, OW-2, M-28A, IP-13 and M-8B) were located within the Phase I test area. Six of these were screened within the shallow A-zone at depths < 20 ft bgs; one well (M-8B) was screened into the deeper formation (23 to 29.5 ft bgs). All wells were monitored on a routine basis as described below (Section 4.3).

Ten (IP-15, IP-16, M-25A, PZ-2, M-23A, M-24A, M-27A, M-29A, P-4A and P-4B) of the seventeen monitoring points were located generally downgradient of the Phase I ISBS treatment area (see Figure 7). Nine of the 10 down-gradient monitoring wells were screened in the shallow A-zone deposits; one well (P-4B) was screened into the deeper formation (21.5 to 31.5 ft bgs).

4.2.4 Injection of Aqueous KMnO_4 Solution

Targeting a loading rate of 4.5 g KMnO_4 per kg soil, 24,050 gallons of aqueous solution containing 3% KMnO_4 (30 g/L or 0.3 lbs/gallon) were injected into the 13 IPs listed on Table 1. Permanganate was injected over a three-day period from September 9-12, 2002. **Appendix C** provides a summary of the field work performed by ORIN Remediation Technologies. The aqueous permanganate solutions were prepared in the field using a municipal potable water supply. Each of the 13 IPs received approximately 1,850 gallons of 3% KMnO_4 solution applied in two events under low pressure (<15 psi) at a rate ranging between 2.5 and 5.5 gallons per minute. As such, each well received approximately 555 lbs of permanganate allowing the material to saturate the A-zone deposits and to migrate downgradient via groundwater flow.

4.3 ISBS Performance Monitoring

The effects of ISBS in terms of NAPL stabilization were assessed through the routine monitoring of 10 wells and the intermittent monitoring of 7 additional wells (**Table 1**). Routine monitoring was conducted approximately every two weeks, resulting in the collection of data eleven times over the Phase I period, which lasted from September 13, 2002 (last day of permanganate injections) through February 22, 2003 (165 days post treatment). Intermittent compliance monitoring for water level and NAPL thickness occurred six times over the Phase I period.

Anticipated ISBS reaction time was two to four weeks. The main objective of the short-term performance monitoring efforts component to the Phase I study was to demonstrate an ability to mitigate NAPL migration to wells within the treated area (*i.e.*, NAPL would stop flowing into the monitoring wells). Routine monitoring of the 10 wells noted above included a variety of field measurements summarized in **Table 3**. Intermittent monitoring consisted of only two field measurements: water level and NAPL thickness. These data described the short-term (<30 days) impacts immediately proximal to the KMnO₄ injection points. If NAPL stabilization could be demonstrated, then longer-term monitoring for decreases in COI in the dissolved phase could be warranted to further validate the concept of flux reduction and source area stabilization.

4.3.1 Sampling and Analysis Procedures

Sampling and monitoring were conducted in general accordance with the Field Activity Plan (URS August 24, 2001). Each of the Site monitoring wells and temporary piezometers was equipped with an expandable locking cap. Prior to commencing water-level data collection or purging operations, each well was inspected for signs of damage, vandalism or unauthorized entry.

All field work, laboratory operations and sample collection activities complied with Beazer's Standard Operating Procedures (SOPs) and data quality assurance previously described (GeoTrans May 4, 2001). Groundwater was measured and analyzed for a variety of physical and biogeochemical parameters (Table 3) using both field and laboratory procedures summarized below:

- Water Level: Prior to purging and sampling wells, the depth to water was measured and recorded as feet below top of casing (fbtoc) for each well using an electrical water-level indicator. To ensure accuracy, the depth to water was observed three times before recording.
- LNAPL/DNAPL Thickness: Prior to purging and sampling wells, the thickness of LNAPL and/or DNAPL was measured and recorded as feet below top of casing (fbtoc) for each well using an electrical oil/water-level indicator.
- Groundwater Field Parameters: Groundwater was removed from the well under low stress conditions (see SOP No.232, Appendix B) using VitonTM tubing. Groundwater entered a flow-through chamber located in front of the pump head. The flow-through cell contained probes (Yellow Springs Instrument [YSI] 3650 or YSI 3800 water quality meter, or equivalent) to

measure water temperature, conductivity, pH, turbidity, dissolved oxygen (DO) and oxidation/reduction potential (redox - Eh). The probes were calibrated prior to field activities (see SOP No. 330). Discharge water was placed in a transportable container for future off-site disposal. Data were obtained once the groundwater monitoring parameters stabilized (*i.e.*, when the change between successive readings of temperature, pH, conductivity, oxidation-reduction potential, and dissolved oxygen were less than 10 percent).

- **Soil Analyses:** Eight soil borings were advanced on May 27, 2003 (the effort was first conducted on April 14, 2003 but the samples were lost during shipping) in the Phase I Treatment Area (**Figure 9**). Five borings (IB-03a, IB-04a, IB-05a and IB-06a) were advanced within the treated area; 2 borings (IB-01a and IB-02a) were located upgradient of the physical barrier and outside of the permanganate area to yield samples that served as untreated controls. Borings were advanced using a 4-inch ID hollow-stem auger to a depth of about 15 ft bgs to the top of the bedrock (B zone). During drilling, field observations were recorded on the boring logs (**Appendix D**). Soil samples (500 g) from each boring location were placed in glass sampling jars fitted with Teflon-lined lids and shipped on ice via overnight courier to the analytical laboratory (Adventus Remediation Technologies/University of Waterloo – Mississauga, Ontario Canada) under standard chain-of-custody procedures. Soils were analyzed for total PAHs/penta via method 8270 and leachable PAHs/penta via modified method 1310.

5.0 RESULTS AND DISCUSSION

The subsurface at the KI Site consists of several distinct lithologic units, summarized as zones A, B, C and D (Figure 5). The conceptual model for the off-property dissolved phase COI plume is horizontal transport in the A-zone and vertical flow into the B-zone. As such, the off-property COI plume is confined within the shallow A-zone aquifer, which extends from the ground surface to approximately 15-ft bgs. The A-Zone consists of cobbly sands with a depth to water of approximately 5-ft bgs to 10-ft bgs. Groundwater in the targeted A-zone aquifer flows east/northeast (Figure 8) at an average horizontal flow velocity of about 1.1 ft/day. Groundwater immediately adjacent to the barrier wall flows in a more northerly direction, approximately parallel to the wall.

5.1 Changes in LNAPL Thickness

Based on the above assumptions of 5 parts KMnO_4 to stabilize 1 part NAPL, (see Equation 3), the introduction of 555 lbs of KMnO_4 is generally sufficient to stabilize approximately 100 lbs, or 13 gallons, of creosote NAPL residual. Over the course of the monitoring period, various field crews noted difficulty in differentiating between creosote LNAPL and spent permanganate that was extracted from the various monitoring points (**Appendix E**). As such, the amount of LNAPL recovered from any monitoring point was non-useful. Hence, changes in LNAPL thickness over time as determined by direct in-well field measurement proved to be the primary measure of ISBS effectiveness.

There was a discernible decrease over time in the thickness of LNAPL for only those monitoring piezometers located within the permanganate treatment area (see **Figures 10 – 13**). For wells located outside of the permanganate treatment area, discernable changes in LNAPL thickness were not detected. Performance monitoring data showed that the LNAPL was not displaced or mobilized downgradient (groundwater flows E/NE per Figure 8). Linear regression analysis on the average LNAPL thickness for four monitoring wells outside the permanganate treatment area (IP-15, M-25A, PZ-2 and M-27A) showed that these values did not change significantly over the 165-day monitoring period (**Figure 14**). Conversely, there was a significant reduction noted when the average LNAPL thickness of seven monitoring wells located within the permanganate treatment area were plotted over time. Based on field notes from the monitoring crews, these changes would be even more significant if spent permanganate did not interfere with the ability to accurately record LNAPL thickness.

5.2 Changes in DNAPL Thickness

The objective of the Phase I ISBS effort was stabilization of LNAPL in the A-zone. As such, discernable temporal changes in DNAPL thickness were not observed (**Figures 15-18**). Similarly, DNAPL thickness data indicated that DNAPL migration did not occur as a result of the permanganate injection (see Appendix E).

5.3 Changes in NAPL Recovery

The change in NAPL recovery in wells completed within the ISBS treatment area provides a quantitative measure of NAPL stabilization. NAPL recovery was performed in five wells within the ISBS for a period of nine months preceding the phase 1 treatment and for nine months following the treatment. Prior to the ISBS treatment, total NAPL recovery within the treatment area was averaging about 2.5 gal/month. After the ISBS treatment, NAPL recovery decreased by greater than 40 percent in four of the five wells.

One well (P-4B) completed across the alluvial (A zone) the upper bedrock (B zone) deposits showed an increase in DNAPL recovery with time. The DNAPL was probably entering the well in the lower portion of the well screen within the B zone. This well is sufficiently down gradient of the Phase One test area that it was not likely influenced by the permanganate injections. Hence, the increase in DNAPL recovery is an indication that the NAPL field measurements can be variable and influenced by a number of uncharacterized factors, including human error.

5.4 Changes in Creosote/Penta Soil Residuals

Additional evidence for the effectiveness of the ISBS approach considered the total mass of creosote/penta residuals in soil. The background (untreated, up-gradient) soil from the 14-15 ft bgs depth interval contained an average (n=2) total PAH concentration of 9,595 mg/kg (**Table 4**). The lower-molecular-weight (LMW), relatively water-soluble constituents represented a majority (7,633.5 mg/kg or 79.5%) of the total PAHs. Soil samples from within the ISBS treatment area at this same approximate depth interval contained an average (n=4) total PAH concentration of 7,771.3 mg/kg. This consisted of 5,997 mg/kg (77%) LWM PAHs and 1,775 mg/kg (23%) of the higher-molecular-weight (HMW) PAH constituents. Comparisons between the treated and background samples indicate a 19% decrease in the total PAH residual mass. Mass of the LMW and HMW

PAHs was reduced by 21% and 10 %, respectively. These data are consistent with those obtained from the complementary laboratory studies, which showed preferential removal of LMW PAHs

Differences in the amounts of PAH leachable from the treated and un-treated soils were much more dramatic. The background soil from the 14-15 ft bgs depth interval contained 40.46 mg/L (n=2) total leachable PAH constituents (**Table 5**). The LMW PAH constituents represented a majority (34.4 mg/L or 85%) of this total. Conversely, soil samples from within the ISBS treatment area at this same approximate depth interval contained only 12.85 mg/L (n=4) total leachable PAHs. This consisted of 12.75 mg/L (>98%) LWM PAHs and only 0.11 mg/L (<2%) of the HMW PAH constituents. Comparisons between the treated and background samples indicate a 76% decrease in the total PAH leachable from the treated soils. Notably, the amount of the HMW PAHs present in the leachate was reduced more than 98%. These data are also consistent with those obtained from the complementary laboratory studies, which showed preferential removal of LMW PAHs via oxidation/dissolution, and stabilization of HMW residuals via physical encrustation/stabilization.

Background soil contained 284.5 mg/kg (n=2) of chlorinated phenol residuals, a majority (236 mg/kg or 83%) of this being penta (**Table 6**). However, soil from the permanganate treatment area contained only 133.8 mg/kg (n=4) total phenols, which included only 115.8 mg/kg penta. It should be noted that sample IB05a had a disproportionately high amount of penta (296 mg/kg total and 80 mg/L leachable), which greatly influenced these results. This represented a 53% reduction in the residual mass of total chlorinated phenols. Interestingly, there were no differences in the amounts of leachable chlorinated phenols between the treated and un-treated soils (**Table 7**). One potential explanation for no change in the amount of leachable chlorinated phenols between treated and un-treated soils is the soil pH. The soil pH ranged from 6.79 (IB01a 14-14.8 ft bgs) to 8.43 (IB05a 14 to 14.5 ft bgs) (**Table 8**). With a pKa for penta of 4.7, more than 99.9% of the penta will be ionized (hence soluble) at soil pH >7. The relative low amount of permanganate added to affect source area stabilization was not apparently sufficient to influence the highly soluble penta at soil boring location IB-05a (see below).

Samples IB03a, IB04a and IB06a were all located within approximately 10 feet of an injection point (Appendix D; Figure 9). Field observations for these borings (Appendix D) indicated the presence of spent permanganate (purplish-brown staining) in these soils. Conversely, boring IBO5a was located about 20 feet from the nearest permanganate injection point, and there was little evidence for permanganate saturation of soils in this area. As applied to the KI Denver Site, it was therefore concluded that permanganate had an effective radius of influence of approximately 15 ft.

Thus, in assessing the potential of ISBS to affect flux reduction and mass removal, we also considered results obtained when data from sample location IB05a were excluded (Tables 4, 5, 6 and 7). Excluding IB05a data, there was a slight increase in the percent mass reduction for total PAHs (from 20 to 33% reduction), but no influence on the reduction of leachable constituents. Considering chlorinated phenol data, exclusion of data from IB05a on the basis that it was outside of the more aggressive treatment zone resulted in higher mass removals (from 53 to 79% removal) and greater reduction in leachable constituents (from 0 to 56% flux reduction). It should be noted that sample IB05a had a disproportionately high amount of penta (296 mg/kg total and 80 mg/kg leachable), which may have influenced these results.

5.5 Field Parameters

Seven wells within the Phase One treatment area (SVW-2, PT-2, M8-B, M8-A, OW-2, M-28A and IP-13) and 10 wells outside of the treatment area (P4-A, P-4B, M-23A, IP-15, IP-16, M-25A, PZ-2, M-27A, M-29A and M-24A) were monitored for the parameters listed in Table 3 from the time of permanganate injection (September, 2002) through the end of the Phase One period (January/February, 2003). Of the various field parameters monitored, redox offered the best indication that the introduction of permanganate influenced the formation (**Appendix G**). In general, the redox potential within the treatment area increased from approximately -100 mV to +300 to +400 mV upon addition of permanganate. As indicated in the field notes, the presence of permanganate interfered with the monitoring of many of the other field parameters. This was especially true for NAPL thickness, as the color and consistency of permanganate and creosote were similar enough to make differentiation in the field difficult. This seemed especially problematic for the quantification of NAPL recovered, as the materials extracted from the wells within the treated plot were often noted as a mixture of spent permanganate (dark purple/black/brown) and possibly creosote.

6.0 CONCLUSIONS

Effective Radius of Influence: As applied to the KI Denver Site, permanganate application had an effective radius of influence of approximately 15 ft.

Changes in NAPL Thickness and Recovery: There was a discernible decrease over time in the thickness of LNAPL for only those monitoring piezometers located within the permanganate treatment area. Changes in DNAPL thickness were not observed suggesting that vertical NAPL migration did not occur. In addition, there was a significant decrease in the amount of NAPL recovered within the ISBS treatment area.

Reduction in Soil Residuals: ISBS yielded a 53% reduction in the residual mass of chlorinated phenols (from 285.4 to 133.8 mg/kg) and a 19% reduction in the mass of total PAHs (from 9,595 to 7,771 mg/kg).

Decrease in Leachable Constituents: Comparisons between the treated and background samples indicated a 76 % decrease in the total PAH leachable (from the treated soils. The HMW PAHs present in the leachate was reduced more than 99% in the treated soils.

Validation of Physicochemical Stabilization Processes Soil analytical data were consistent with those obtained from the complementary laboratory studies which showed preferential removal of LMW PAHs via oxidation/dissolution and stabilization of HMW residuals via physical encrustation/stabilization

Cumulatively, laboratory and field data validated the effectiveness of the ISBS process and its ability to reduce the flux of PAHs/penta into the dissolved phase. Flux reduction should have a significant beneficial affect thereby accelerating the contraction of the dissolved phase COI plume at the KI Denver Site.

7.0 REFERENCES

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TABLE 2. SUMMARY OF MONITORING WELLS FOR PHASE I FIELD TESTING.

Well ID	Description of Monitoring Well		Comments
	Top of Screen (ft amsl / ft bgs)	Bottom of Screen (ft amsl / ft bgs)	
KMnO4 Area			7 well locations 1 Temporary IP + 6 Existing Monitoring Wells (See Figure 7)
SVW-2	5212.0 8.2	5201.5 17.9	Routine monitoring ten times over the Phase I period. Decreases in NAPL thickness will validate source area stabilization.
M-8A	5214.8 4.5	5204.8 14.5	As above
PT-02	5212.2 7.5	5202.2 17.5	As above.
OW-2	5212.0 7.5	5202.0 17.5	As above.
M-28A	5208.41 15.25	5203.41 20.25	As above
IP-13	5206.74 17	5201.74 22	As above
M-8B	5196.6 23	5190.1 29.5	Deep monitoring well. Routine monitoring. Decreases in NAPL thickness will validate source area stabilization.
Downgradient of Treatment Area			10 Well locations 2 Temporary IP + 8 Existing Monitoring Wells (See Figure 7)
IP-15	5205.24 15.5	5202.24 18.0	Routine monitoring ten times over the Phase I period. Data describe the short-term (<30 days) impacts immediately proximal to the points of KMnO4 additions. Future decreases in COI in the dissolved phase will validate source area stabilization.
IP-16	5207.61 11	5202.61 16	As above
M-25A	5206.09 12.3	5201.09 17.3	As above.
PZ-2	5212.40 6	5202.40 16	Intermittent compliance monitoring for water level and NAPL thickness only six times over the Phase I period
M-23A	5205.61 10.4	5200.61 15.4	As above
M-24A	5206.60 10.7	5201.60 15.7	As above
M-27A	5206.41 16.7	5201.41 21.7	As above
M-29A	5208.07 9.3	5203.07 14.3	As above
P-4A	5212.5 5	5202.5 15	As above
P-4B	5196.1 21.5	5186.1 31.5	Deep well. Intermittent compliance monitoring for water level and NAPL thickness only

TABLE 1. SUMMARY OF INJECTION POINTS FOR PHASE I FIELD TESTING.

Well ID	Top of Casing Elevation (ft amsl)	Top of Screen (ft bgs)	Bottom of Screen (ft bgs)
IP-01	5222.16	13.30	18.30
IP-02	5221.62	13.50	18.50
IP-03	5222.27	11.00	16.00
IP-04	5222.30	13.80	18.80
IP-05	5222.73	12.30	17.30
IP-06	5222.52	11.20	16.20
IP-07	5221.77	10.30	15.30
IP-08	5221.22	13.50	18.50
IP-09	5221.77	12.20	17.20
IP-10	5221.52	12.00	17.00
IP-11	5221.52	11.30	16.30
IP-12	5225.70	15.00	20.00
IP-13	5226.98	17.00	22.00
IP-14	5226.34	17.50	22.50
IP-15	5225.16	15.50	18.00
IP-16	5222.46	11.00	16.00
IP-17	5222.27	13.30	18.30

Notes: A total of 17 Permanganate injection points (IP) were installed August 20-23, 2002. Permanganate was applied to 13 of these IPs. Wells IP-04, IP-13, IP-15 and IP-16 were used for monitoring purposes and did not receive permanganate.

TABLE 3. GROUNDWATER QUALITY AND PHYSICAL MONITORING PARAMETERS FOR RECORDING THE AFFECTS OF ISBS AT THE KI DENVER SITE.

Matrix	Analysis	Method	Data Use	Analysis Type
Water	pH	Field pH – Meter	Range acceptable for biological activity	Field Analysis
Water	Oxidation-reduction potential	Field Probe	<10 mV indicates anaerobic conditions; Indicator of oxidation reactions.	“
Water	Dissolved Oxygen	Field DO Meter	<1.0 mg/l indicate anaerobic conditions; Indicator of oxidation reactions	“
Water	Turbidity	Field Meter	Indicator of chemical fouling	“
Water	Temperature	Field Meter	Indicator of chemical reactivity and biodegradation parameter	“
Water	Conductivity	Field Meter	Water mixing	“
Water	Total Mn	HACH	Presence of oxidant KMnO ₄	“
Water	Groundwater Level	Field Water-level probe	Indicator of groundwater flow direction.	“
Water	NAPL Recovery	Peristaltic Pump	Measurement of Free-Phase NAPL Volume	“
Water	LNAPL / DNAPL Thickness	Filed Oil / Water indicator probe	Measurement of NAPL presence	“
Soil	NOD, Total PAH/Penta, leachable PAH/Penta	8270 and 1310 (modified)	Residual organic impacts and flux reduction	Laboratory Analysis

APPENDIX A

**Technical Memorandum December 4, 2001
Natural Oxidant Demand**

APPENDIX B

**Technical Memorandum December 5, 2001
Oxidant Soil Loading Demands for Stabilization**

APPENDIX C

Summary of Work Performed by ORIN September 7-14, 2002

APPENDIX D

Post Treatment Soil Boring Logs for Residual Soil Testing

TO BE PROVIDED BY GEOTRANS

APPENDIX E

Summary of NAPL Thicknesses

APPENDIX F

Laboratory Report – Soil Residual Testing

APPENDIX G

Summary of Field Parameters