

INNOVATIVE COUPLED CHEM-BIO TREATABILITY STUDY LEADING TO LARGE SCALE PILOT TEST AT A WOOD TREATING FACILITY

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ABSTRACT

Operations at an active wood treating facility (Site) in Mississippi resulted in a semi-volatile organic compound (SVOC) soil and groundwater plume exceeding 500 meters (m) in length and 150 m in width. SVOC constituents include Pentachlorophenol, Naphthalene, and fourteen other SVOCs. The lead regulatory agency agreed that limited active remediation is likely adequate to support a dominant monitored natural attenuation (MNA) remedy. Three subsurface regions along the centerline of the plunging plume are areas of concern due to elevated groundwater impacts and for these three areas in-situ soil and groundwater treatment to reduce dissolved-phase SVOCs were deemed appropriate.

A coupled chemical oxidation and enhanced aerobic bioremediation (“Chem-Bio”) pilot testing strategy was developed and initiated with a relatively comprehensive bench-scale treatability study. The treatability study, conducted during the winter of 2006-2007, was successful in evaluating the efficacy of the Chem-Bio strategy in the presence of highly challenging geochemical conditions. Specific application requirements and potential field-scale effectiveness was estimated for two remediation products manufactured by FMC Corporation: PermeOx® Plus and OBC.

The Site is underlain by a thick sequence of alluvium, coarsening with depth within the horizon of interest (i.e., 12 to 34 m-below ground or m-bg). The most contaminated soil samples contained 3,400 mg/kg of total organic carbon (TOC) and 448 mg/kg of chemical oxygen demand (COD). Total detected SVOC concentrations exceeded 500,000 ug/Kg. The soil had an acidic pH of 3.8 and required 2.9 g sodium hydroxide per kg of soil to bring the pH up to 11. The soil and distilled water had a negative oxidation-reduction potential (ORP) of -38 mV. The groundwater had a COD of 46 mg/L, a pH of 4.3, ORP of 24 mV, and total detected SVOC concentrations exceeded 100,000 ug/L.

Soil oxidant demand tests were conducted as well as long-term destruction removal efficiency (DRE) tests. OBC was used to promote sequential chemical oxidation (via alkaline activation of sodium persulfate) and enhanced biodegradation (via slow oxygen release). PermeOx® Plus, an engineered calcium peroxide product for timed oxygen release, also provides alkalinity to activate the persulfate in OBC. PermeOx® Plus was also tested separately to evaluate the potential for enhanced bioremediation of the full-strength soils and groundwater and of 10:1 diluted soils and groundwater. The diluted treatments were included to assess the potential for 1)

biological polishing post-chemical oxidation and 2) treatment of less impacted regions of the groundwater plume. Phospho-lipid fatty acid (PLFA) analyses were conducted to evaluate the impact of both chemicals on native micro-ecology. After 64 days, OBC resulted in 23% and 40% reductions in total SVOCs in soil and groundwater, respectively. After 94 days, undiluted SVOC reductions for soil and groundwater amended with PermeOx® Plus were 70% and 71%, and 76% and 83% for the diluted soil and groundwater. Despite significant chemical loading required by the highly contaminated soil and groundwater, only a temporary one-log depression in overall viable biomass as measured by PLFA was observed and in all cases the microbial population rebounded with an advantageous shift in the specific types of microorganisms.

A one-year duration pilot test involving the three areas of concern was started May 2007. The geochemical and SVOC DRE of OBC injected into PermeOx® Plus modified groundwater is being monitored at field scale. If significant contaminant reductions are observed during the pilot test period as a result of chemical oxidation and subsequent aerobic bioremediation, then additional limited treatment may be pursued. Once active treatment is terminated, the project team expects that anaerobic conditions will re-establish. It is speculated that information on the nature of that future transition and whether the active treatments ultimately detract from or contribute to (as they are expected to do) subsequent natural attenuation processes will require at least several additional years of groundwater monitoring.

INTRODUCTION

The concept of coupled chemical oxidation and bioremediation for soil and groundwater treatment to reduce anthropogenic organic pollutants is receiving increasing attention in academia and the consulting engineering and contracting communities (Huling and Pivetz, 2006; ITRC, 2005). The reason that the concept is gaining momentum is that stand-alone treatment technologies, conventional and innovative alike, are often observed to be significantly deficient when applied to environmentally impaired properties that include complex hydrogeology, recalcitrant contaminant types and phases, and/or stringent remediation objectives. The “Chem-Bio” concept involves potentially numerous and complex physical, chemical, and biological phenomena. But at the basic level, there is a sequential process of natural organic matter and anthropogenic organic contaminant destruction by chemical oxidation reactions followed by some form of biodegradation enhancement that is enabled by local modifications to existing geochemical conditions and chemical oxidation reaction by-products. The obvious follow up to chemical oxidation is aerobic biodegradation enhancement due to the chemical oxidation induced soil-groundwater system ORP elevation and DO (DO) addition. This is the case for chemical oxidation technologies based on catalyzed hydrogen peroxide or ozone. Depending on the activation method chosen, this can also be the case where sodium persulfate is used. Compared to chemical oxidation or aerobic bioremediation as stand-alone technologies, the coupling of these technologies offers the potential for technologically and economically superior remedial actions that result in kinetically more rapid contaminant destruction, destruction of a wider range of contaminants, as well as destruction over a larger spatial scale, and ultimately achievement of lower end-point contaminant concentrations.

All coupled chemical oxidation and enhanced aerobic biodegradation treatment campaigns involve a planned or unplanned transition from active oxygen input to a state where oxygen input, if any, is due solely to natural processes. Once active oxygen application is suspended, site

geochemical and microbial conditions will change. The geochemical and microbial setting may remain dominantly aerobic, but often will return to anaerobic conditions. The degree of geochemical-microbial shift that eventually occurs is a function of several independent and dependent factors and is difficult to predict *a priori*. The significance of these shifts to a post-active treatment status, where natural attenuation processes make contributions of further contaminant mass or concentration reduction, is perhaps even more difficult to predict. More research is necessary to improve our collective understanding of the processes alluded to above and how these processes might be leveraged for additional benefit.

Anaerobic environments can develop naturally post-chemical oxidation treatment (Droste, et. al, 2002). However, the intentional coupling of chemical oxidation with anaerobic biological processes, oxidative or reductive, is only now becoming the focus of research and development. For example, the use of sodium persulfate in a chemical oxidation reaction can promote subsequent anaerobic conditions via several mechanisms and optimization of some or all of these mechanisms to achieve continued contaminant reduction is possible. Fundamentally, dissolved organic carbon will increase as well as sulfate. Sulfate reducing bacteria (SRB) can be stimulated by the availability of sulfate. Fermentation of the dissolved organic carbon (DOC) resulting in molecular hydrogen production can occur. Both SRB and reductive dehalogenation reactions can be promoted by the presence of molecular hydrogen and sulfate reduction can accelerate reductive dehalogenation (Suflita, et al., 1998). These reactions can occur even after strong oxidative conditions from a coupled chemical oxidation and aerobic biodegradation phase have developed and subsided. These reactions can be controlled from an engineering perspective and thus it is reasonable to consider the potential for improved treatment outcomes relative to contaminated properties ranging from those impacted by petroleum hydrocarbons, chlorinated solvents, or a mixture of both categories of contaminants of concern. This is an area of active applied research and development and it is anticipated that significant knowledge and capability gains will be experienced over the next several years.

Rigorous site characterization and treatment engineering improves the probability of successful outcomes when any class of in-situ remedial technology is considered and this is the case for chemical oxidation, bioremediation, and certainly the coupling of these two technology classes. Tools that are available for developing rigorous full-scale treatment programs include site conceptual modeling, quantitative modeling (analytic and numerical), bench-scale treatability studies, and field pilot tests. None of these tools are without their weaknesses, but practitioners using these tools alone or in some combination are able to reduce uncertainties and ultimately the risk of project failure.

The remainder of this paper presents a case study that highlights the use of bench-scale treatability protocols to evaluate an innovative “Chem-Bio” strategy considered for field application at a wood treating facility located in the State of Mississippi, United States of America. The chemical oxidation and enhanced aerobic biodegradation components of the process were decoupled in the laboratory to meet project budget and schedule constraints. Despite the non-ideal test conditions, the treatability study was successful in showing process efficacy and providing a design basis for a subsequent field pilot test that initiated in the spring of 2007. As of this writing, two separate chemical injection events involving application of FMC Corporation products OBC and PermeOx® Plus have taken place and approximately seven

months of a yearlong performance-monitoring phase has been completed. This paper concludes with a summary of treatability study conclusions and selected preliminary observations from the field pilot test as well as a general discussion concerning the coupled chemical oxidation and bioremediation concept.

SITE BACKGROUND

The case study site is an 1225-acre active wood treating facility located near the town of Wiggins, Mississippi, United States of America. Wiggins is approximately 50 miles north of the Gulf of Mexico coast and is situated on a lower coastal plain with a pine-dominated forest growing within acidic soils. Annual precipitation is approximately 55 inches per year (140 cm per year). The surface geology consists of clays, sands, and gravels of late Tertiary age (Stewart, 2003).

Figure 1 is a site plan showing the active operations area of the facility. The dimension of the north property line is approximately 3300 feet (1006 m) and that for the west boundary is approximately 3100 feet (945 m). Plan details include traces of surface features including roads, buildings, and waste disposal ponds closed according to regulatory permit requirements. Wood treating chemicals at the Site include Pentachlorophenol (PCP), chromated copper arsenate (CCA), and (now discontinued) creosote. Church House Branch, a small intermittent tributary to the Pascagoula River, crosses the property from northwest to southeast. The reach of this stream coincident with the property is losing at times of higher precipitation and runoff and gaining at times of low base flow.

Figure 1. Site Plan – Active Operations Area with PCP Plume as of 2006

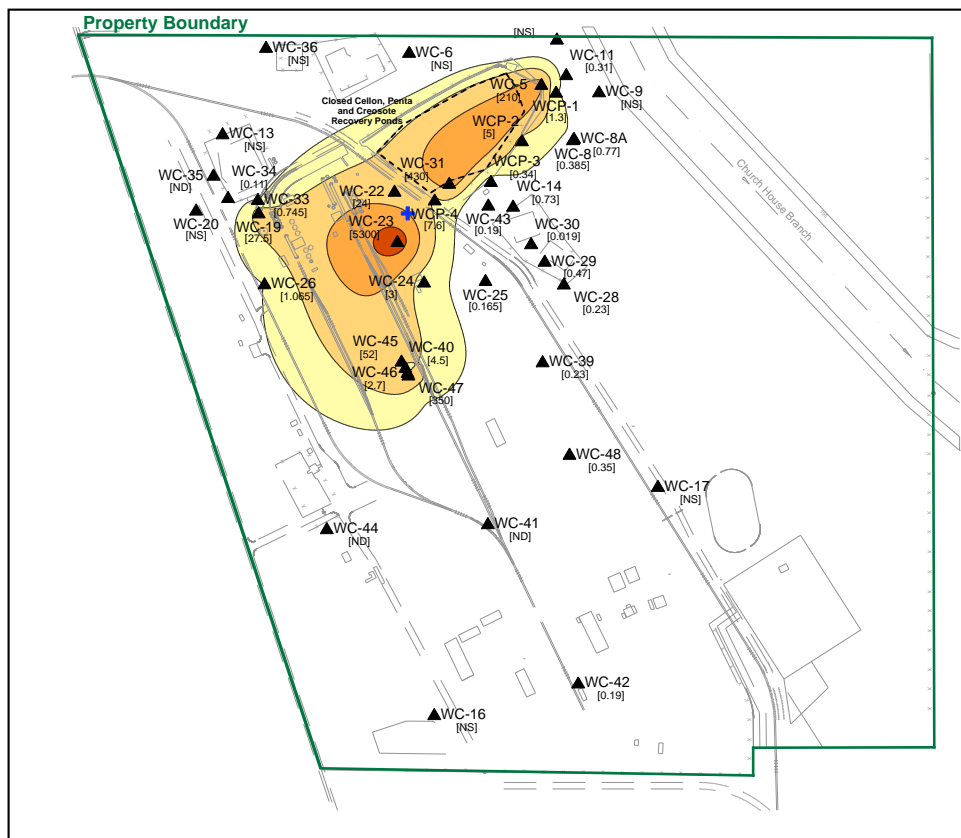
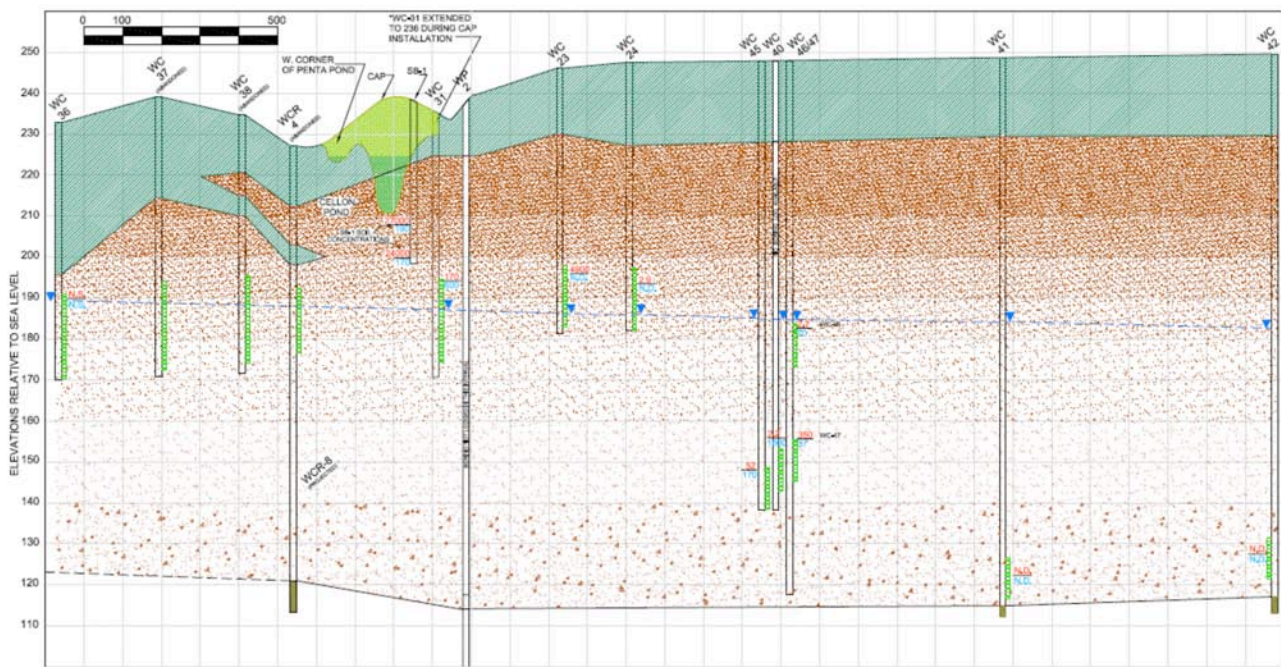


Figure 1 also shows the layout of the groundwater monitoring well network as it existed prior to late 2006 design data collection efforts carried out in support of the subject treatability study and pilot test. Early 2006 measurement data indicate a maximum potentiometric head difference across the property from north to south (the general direction of groundwater flow) was 10.5 feet (3.2 m) for a relatively low lateral hydraulic gradient of 3.4×10^{-3} ft/ft (or m/m). The distribution of aqueous phase PCP as of 2006 is shown.

The Site is underlain by a thick sequence of alluvium, coarsening with depth within the horizon of interest (i.e., 12 to 34 m-bg). Encountered within this horizon are the major formations of Pascagoula and Citronelle (Figure 2, scale in feet). Low permeability Citronelle soils cover the Site and are underlain by permeable Citronelle soils, underlain in turn by the Pascagoula Aquitard (encountered approximately 110 ft bg). The depth to the water table is between 40 and 60 ft bgs depending on topography.

Figure 2. Hydrogeologic Profile



Soil and groundwater within the Citronelle Formation are impacted by wood treating chemicals and their natural breakdown products. In the vicinity of the closed waste disposal ponds (general location indicated in Figure 2), non-aqueous phase liquids (possibly creosote) have been observed as well as heavily stained soil. As a general grouping of contaminants, semi-volatile organic compounds (SVOCs) including Polyaromatic hydrocarbons (PAHs) are of concern. PCP and naphthalene are two key Chemicals-of-Concern (CoC) present in soil and in the groundwater plume that has been delimited across much of the active operations area. Considering all groundwater constituents the groundwater plume exceeds 500 meters (m) in length and 150 m in width. Soil and groundwater in the vicinity of the closed ponds and hydraulically down gradient from those ponds are relatively acidic and exhibit relatively high total organic carbon (TOC) and chemical oxygen demand (COD).

The background geochemistry and microbial ecology operate under relatively highly aerobic conditions. However, within the groundwater plume it appears that the full range of electron acceptors (e.g., oxygen, nitrate, manganese, iron, sulfate, and carbon dioxide) and electron donors (i.e., organic carbon, contaminants) have been utilized by native microorganisms resulting in spatially and temporally variable reducing conditions. Relatively low DO, high dissolved iron, high dissolved methane, and chloride (a mineralization product of PCP for example) point to the activity of intrinsic attenuation processes of biodegradation and perhaps abiotic processes. These processes appear to be most important beneath and in the vicinity of the closed waste disposal ponds.

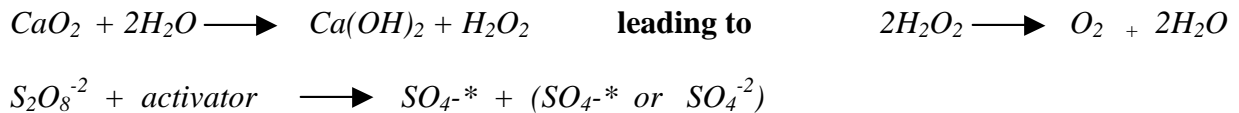
FOCUSED TREATMENT STRATEGY IN SUPPORT OF A FUTURE MNA ACTION

With the support of Premier Environmental Services, Inc. (Premier), the property owner demonstrated to the state regulatory agency that the dissolved-phase plume was undergoing significant natural attenuation and was essentially stabilized. The regulatory agency in accepting that natural attenuation was occurring and likely effective, requested that the property owner take measures to further reduce the risk of migration and resource impact as well as the time for natural attenuation processes to effectively treat the groundwater. Three general subsurface locations of known elevated aqueous PCP and/or naphthalene concentrations or “hot spots” along the plume centerline were identified for field pilot testing of one or more technologies potentially capable of being used to reduce contaminant mass/concentrations in a way that would be compatible with site natural attenuation processes. Each hot spot surrounds the screened interval of a certain monitoring well and is referred to by that well’s designation. The up gradient hot spot is called WC-5 and is located at and immediately below the water table at the up gradient edge of closed waste disposal ponds. Hot spot WC-23 is also at and below the water table at a location approximately 250 feet (76 m) down gradient of the closed ponds. Finally, hot spot WC-40 is generally coincident with the plume axis as it plunges downward some 30 feet (9.1 m) below the water table. WC-40 is approximately 500 feet (152 m) down gradient of the closed ponds.

Premier and their subconsultant AMEC Earth & Environment (AMEC) chose to pursue a coupled chemical oxidation and oxidative bioremediation strategy for the two hot spots closer to the closed waste disposal ponds (WC-5 and WC-23) and enhanced aerobic bioremediation for the down gradient and deeper hot spot WC-40. They also decided to conduct a detailed bench-scale treatability study using site soil and groundwater samples prior to proceeding to pilot testing. In this way, technology of interest could be cost-effectively tested for efficacy and to develop a pilot test design basis. A technology-screening task was performed and in-situ direct push injection of base-activated persulfate for chemical oxidation and solid-phase timed-release oxygen for enhanced aerobic biodegradation were chosen for further evaluation. Activated persulfate was chosen because of its potential to rapidly and completely chemically oxidize most or all of the PCP and PAH contaminants. Additionally, persulfate degrades to the alternative electron acceptor sulfate. For this site, sulfate addition might enhance SRB activity and reduce further mass via oxidative biodegradation. Base activation under high alkalinity was selected as the activation technique due to the robust sulfate radical generation environment that is created when the aqueous pH exceeds approximately 10 s.u. Other benefits of base activation include simultaneous In-Situ NOM Extraction™ (i.e., the extraction of finite amounts of natural organic

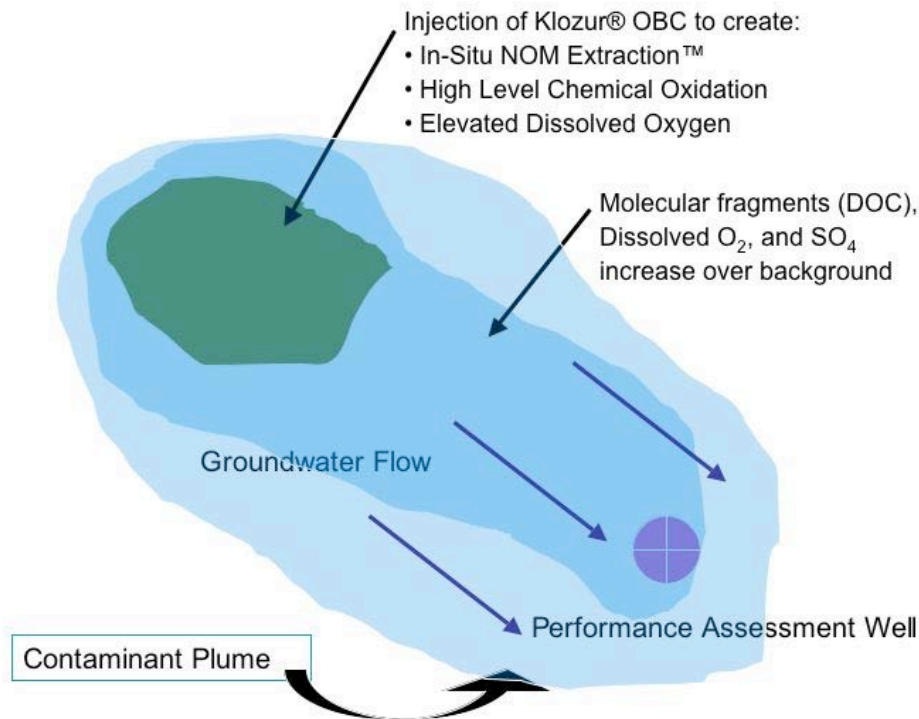
matter and associated sorbed phase contaminants) from mineral surface sorption sites into the aqueous phase. Once in the aqueous phase, the NOM (and contaminants) are more available for partial or complete chemical oxidation breakdown and subsequent utilization in biologically mediated reactions (Gates and Siegrist, 1995). Depending on the alkalinity-contributing material used for activation, oxygen can be a by-product and this is a benefit for sites like the subject site involving aerobically degradable contaminants. Once chemical oxidation and oxygen have altered the geochemistry of the treatment zone, a solid-phase timed-release oxygen source can be applied as needed to maintain enhanced aerobic biodegradation rates.

Premier and AMEC chose two peroxygen products manufactured by FMC Corporation for treatability testing purposes and, if appropriate, field pilot testing. PermeOx® Plus was chosen as the timed oxygen release product consisting of engineered calcium peroxide. The product OBC was chosen as it is the only product designed to produce a sequentially-coupled chemical oxidation and aerobic biodegradation treatment effect involving base activation of sodium persulfate. The base activator in OBC is PermeOx® Plus. Selected chemical reactions are summarized as follows:



The general strategy for field deployment of these products is illustrated in Figure 3.

Figure 3. Conceptualization of Coupled Chemical Oxidation - Oxidative Biodegradation



Important considerations when simulating coupled chemical oxidation and bioremediation processes in laboratory microcosms are the relatively involved test protocols, the time required to achieve a meaningful result (typically driven by microbial reaction-lag-adjustment-growth dynamics) as well as associated costs. The subject project involved constraints that did not allow for a fully coupled laboratory evaluation. Instead, a decision was made to de-couple the two basic processes and evaluate each individually and simultaneously. The chemical oxidation testing involved a Total Oxidant Demand (TOD) phase and a Destruction Removal Efficiency (DRE) phase, in both cases using full strength soil and groundwater collected from near the closed ponds. The oxidative bioremediation testing involved a DRE phase using the same full strength soil and groundwater. To assess the influence of reduced contaminant concentrations on bioremediation processes, DRE testing was also performed using 10:1 diluted soil and groundwater. Although far from simulating a true coupled affect, it was decided that the diluted samples would provide useful efficacy and design basis information that could be applied to subsequent consideration of both the coupled process at field scale and to possible bioremediation in the periphery of the plume.

TREATABILITY STUDY DESIGN

The experimental design for the bench-scale treatability study consisted of four phases of work:

1. Initial characterization of the site soil and groundwater;
2. Estimation of total oxidant demand (TOD) using the OBC product;
3. Evaluation of the chemical oxidant destruction removal efficiency; and
4. Evaluation of the effectiveness of PermeOx® Plus to promote aerobic biodegradation of the PCP, naphthalene, and other semi-volatile organic constituents found at the site.

Phase I, Initial Characterization of Site Soils and Groundwater

Sample Acquisition. On November 5, 2006, a geoprobe direct push rig and sampling tools were used to retrieve two (2) quart amber glass jars of soil from immediately below the water table near the closed ponds. Eight (8) quart amber glass jars of groundwater were obtained from the same boreholes from which soil was retrieved. This sample volume was sufficient to conduct initial sample characterization and the chemical oxidation and biodegradation experiments. Initial characterization methods and results are described below.

Methods. The soil samples were screened to remove debris and mixed by hand to apparent homogeneity. The soil was analyzed for SVOCs by EPA 8270, TOC COD. The groundwater was analyzed for SVOCs by EPA 8270.

Results. The soil contained 3,400 mg/kg of TOC and 448 mg/kg of COD. Twenty grams of soil diluted with 100 mL of distilled water had an acidic pH of 3.8 and required 1.45 mL of 1 N sodium hydroxide to bring the pH up to 11. The sodium hydroxide demand was 2.9 g per kg. The soil and distilled water had a negative ORP of -38 mV. With concentrations in units of ug/kg, the soil contained 2,4-dimethylphenol (360 J) PCP (1500 J), naphthalene (120,000), acenaphthylene (1000 J), acenaphthene (62,000), fluorine (46,000), phenanthrene (130,000), anthracene (13,000), fluoranthene (60,000), pyrene (37,000), benzo(a)anthracene (8600),

chrysene (7500 J), benzo(f)fluoranthene (2100), benzo(k)fluoranthene (2400), benzo(a)pyrene (2100), and benzo(g,h,i) perylene (430 J). Other SVOCs may be present, but were not detected at the dilutions employed for these analyses.

The groundwater had 46 mg/L of COD as measured using the Hach method. The pH of the groundwater was 4.3 and the ORP was 24 mV. The ORP is believed to be artificially high due to sample handling. The only SVOC constituents detected in the groundwater were 2,4,6-trichlorophenol at 60 ug/L (J code) and PCP at 4900 ug/L.

Phase II, Determination of Total Oxidant Demand

In addition to reacting with many hazardous chemicals, persulfate will react with many organic and inorganic materials naturally present in site soils. If the concentrations of these non-target oxidizable materials are very high, large amounts of oxidant will be required for field treatment, resulting in high full-scale implementation costs. The total oxidant demand (TOD) test is designed to evaluate the oxidant demand exerted by both site soils and contaminants. TOD results are also used to select oxidant dosage level(s) for subsequent DRE testing.

Methods. An initial estimate of the OBC that might be effective at field scale was developed using the FMC OBC stoichiometric calculator and site data to be 15 gm/kg soil, a relatively high value compared to most sites. Because radical chemistry is not considered when using the FMC OBC calculator, the indicated dosage levels can be conservatively high in some cases. A range of OBC dosage levels surrounding this value of 15 gm/kg was selected for bench-scale testing using 40 g soil as the basis. The range is 0.45 g, 0.6 g, and 0.75 g. Tests were performed by adding 40 grams of wet-weight processed soil to each of six 250-mL (8 oz) bottles. Two bottles were amended with 0.45 g OBC, the soil and OBC mixed as thoroughly as possible, and 100 mL of tapwater added; two bottles were amended with 0.6 g OBC, the soil and OBC mixed as thoroughly as possible, and 100 mL of tapwater added, and two bottles were amended with 0.75 g OBC, the soil and OBC mixed as thoroughly as possible, and 100 mL of tapwater added. The bottles were shaken on a rotary shaker. After 48 hours, the soil was allowed to settle and the aqueous concentration of persulfate determined by addition of 0.4 N ferrous ammonium sulfate and back titration with 0.5 M potassium permanganate solution. The quantity of oxidant remaining in solution was determined by subtracting the quantity of permanganate used in a blank from the quantity of permanganate used for the sample. The pH and ORP of the aqueous phase was determined. The natural oxidant demand was calculated.

Results. The initial OBC concentrations were calculated to be between 4,491 and 7,515 mg/L or 11,222 and 18,703 mg/kg soil. By Day 1, the pH of the treatments with the lowest loading of OBC had fallen to between 9.8 and 9.9. These bottles received 0.15 to 0.2 mL of 1 N sodium hydroxide to bring the pH back to 10.4 to 10.5. On Day 2, the pH had fallen to between 9.4 and 10.0 at the lowest and medium OBC loadings. A pH of 10.9, within the optimal range for alkaline activation of the persulfate, was found at the highest loading of OBC. The OBC concentrations were measured to be between 1,633 and 3,025 mg/L. The average TOD ranged from 6.9 g/kg soil for the lowest loading to 11.1 g/kg soil for the highest loading.

Phase III, Determination of Chemical Oxidant Destruction Removal Efficiency (DRE)

Methods. The DRE test is designed to investigate the effectiveness of OBC to oxidize the soil and groundwater contaminants within a given period of time, in this case an unusually long 64 days. Four 500 mL (16 oz) bottles (A-D) were prepared with 100 g soil and 250 mL groundwater amended with the 2 g OBC at a 20 g OBC/kg soil dosage selected based on the results of the TOD test. A fifth bottle (E) received 100 g soil and 250 mL groundwater without the oxidant and was sacrificed immediately. The remaining samples were placed onto a rotary shaker at moderate revolutions per minute setting.

SVOC analyses were performed on the following samples: (1) untreated control (Time =0) soil and groundwater, (2) the treated groundwater after 1 day of reaction, (3) the treated groundwater after 8 days of reaction, (4) the treated groundwater and soil after 29 days of reaction, and (5) the treated soil and groundwater after 64 days. On day 50, the pH of the remaining bottle D was adjusted to pH 11 with 0.48 mL of 10 N sodium hydroxide. In addition, a soil sample of Bottle C at Day 29 was analyzed for PLFA by Microbial Insights of Rockford, Tennessee, USA. The biomass quantity in a particular sample as well as the identity of many of the constituents of the biomass can be determined with considerable accuracy by their unique pattern of phospholipids fatty acids. Certain biomarkers also can identify stress or slowed growth and decreased permeability of the microbial cell walls. Groundwater samples were concurrently analyzed for pH, temperature, DO, persulfate, and ORP. All SVOC samples were cooled and shipped on ice to the analytical laboratory,

Results. The initial loading of OBC was 7,974 to 7,994 mg/L OBC or 19,960 to 20,020 mg/kg soil. The pH of the soil and groundwater without the OBC was 4.3, the ORP was 257 mV, the temperature 18.4 °C, and there was a DO content of 8.6 mg/L (slightly below saturation of 9.5 mg/L). After one day in contact with OBC, the pH had fallen to 10.4 in bottle A. The ORP was 70 mV, the temperature 21.1 °C, DO 8.3 mg/L (below saturation of 9.0 mg/L), and the OBC was 4,649 mg/L, a decrease of 42% in 24 hours. On Day 8, the pH had fallen to 8.5, the ORP was 163 mV, and there was 9.5 mg/L of DO (slightly more than saturated levels of 8.8 mg/L as the PermeOx® Plus released oxygen) at the temperature of 22.4 °C. The OBC had declined to 3,257 mg/L, a decrease of 59% from the initial levels. By Day 29, the pH had fallen to 7.3, the ORP was 182 mV, the temperature was 21.5 °C, and there was 9.4 mg/L of DO (again slightly above normal saturation levels). The OBC was the same as measured on Day 8 (3,257 mg/L). On Day 50, the pH was adjusted to 11 with 0.48 mL of 10 N sodium hydroxide. The remaining Bottle D was sampled on Day 64. The pH again had decreased to 8.8, the ORP was 124 mV, temperature 21.0 °C, and there was 7.4 mg/L of DO (undersaturated). The OBC concentration was 1,865 mg/L, a decrease of 77% over the two month long incubation period. Significant concentrations of persulfate persisted over 2 months. The total oxidant demand over the 64-day incubation period was 15.3 g/kg.

The PLFA of the soil was measured initially in one of the biodegradation test controls. There were 2.08×10^7 cells/g based upon the recovery of PFLA from the soil; this indicates relatively high numbers of microbes. Most of the microbes were Proteobacteria (48.0%) and Firmicutes/anaerobic gram negative (26.2%) with lesser numbers of anaerobic metal reducers (7.4%), sulfate reducing bacteria (SRB) and actinomycetes (4.6%), general bacteria (10.2%), and

3.6% eukaryotes. The ratio of slowed growth was 0.88 and none of the bacteria had decreased permeability. After 29 days incubation, the total biomass declined to 2.7×10^6 cells/g, possibly due to the alkaline conditions. The percentage of firmicutes/anaerobic gram negative, anaerobic metal reducers and SRB/actinomycetes declined as the soil and groundwater became more aerobic. There were increases in percentage of the Proteobacteria and General bacteria. The ratio of organisms with slowed growth and decreased permeability increased, again possibly due to the alkaline conditions.

The initial soil sample contained high levels ($>100,000$ $\mu\text{g}/\text{kg}$) of phenanthrene, moderate levels (10,000 to 100,000 $\mu\text{g}/\text{kg}$) of naphthalene, 2-methylnaphthalene, acenaphthene, dibenzofuran, fluorene, anthracene, fluoroanthene, pyrene, and benzo(a)anthracene and lower levels ($<10,000$ $\mu\text{g}/\text{kg}$) of PCP, n-nitrosodiphenylamine, carbazole, chrysene, benzo(b)fluoranthene, benzo(k)fluoranthene, and benzo(a)pyrene. In the soil phase, PCP and n-nitrosodiphenylamine were reduced to below the detection limits within 29 days. After 64 days, anthracene, carbazole, benzo(a)pyrene, and indeno(1,2,3-cd)pyrene were non-detect. The concentrations of the following compounds were reduced by more than 50% over the 64 day treatment interval: PCP, acenaphthene, fluorene, n-nitrosodiphenylamine, anthracene, carbazole, benzo(a)anthracene, and benzo(a)pyrene. The remaining SVOCs were less extensively attacked. The overall concentrations of total SVOCs in the soil were reduced by 37%.

The groundwater contained many of the same SVOCs as found in the soil including moderate levels ($>1,000$ $\mu\text{g}/\text{L}$) of naphthalene, 2-methylnaphthalene, and acenaphthene, and lower levels ($<1,000$ $\mu\text{g}/\text{L}$) of 2-methylphenol, 4-methylphenol, 2,4-dimethylphenol, PCP, acenaphthylene, dibenzofuran, fluorene, phenanthrene, anthracene, carbazole, fluoroanthene, and pyrene. Within one day, most of the PCP in the soil moved into the aqueous fraction due to the high pH. There was little treatment by the OBC in the first day. Over the first 8 days, the PCP levels declined as did the concentrations of most of the SVOCs. There was a 40% drop in the total phenols and SVOCs over the first 8 days. Little further reduction occurred over the next 56 days, possibly as a result of the pH being lower than optimal for the activation of the persulfate and enhanced bio-activity had not yet been expressed. The following compounds were reduced by $>50\%$ in the aqueous phase over the 64 day incubation period: 2-methylphenol, 4-methylphenol, 2,4-dimethylphenol, PCP, acenaphthene, fluorene, carbazole, fluoranthene, and pyrene. The overall percent removal of SVOCs in the aqueous phase was 33.5%.

Phase IV, Determination of Biotreatability DRE

Methods. The processed soil and groundwater were evaluated to determine the ability of PermeOx® Plus to promote the aerobic biodegradation of the contaminants. An initial estimate of the PermeOx® Plus that might be effective at field scale was developed using the FMC PermeOx® Plus calculator, site data, and a stoichiometric uncertainty factor of 2.0 to be 35 gm/kg soil. As was the case for the initial OBC dosage estimate, the highly aggressive site conditions factored into selection of an unusually high PermeOx® Plus dosage amount. For 200 g soil in microcosms this translates into 7.0 g PermeOx® Plus.

Soil/groundwater water slurries were constructed in 500-mL (16-oz) bottles. Two thousand two hundred mL of groundwater were combined in a 2,800 mL jug. To each of five bottles, 200

grams of soil were added and 7.0 g PermeOx® Plus. The bottles were filled with approximately 350 mL of groundwater, the bottles capped, and mixed by hand. The weights of the bottle, soil, PermeOx® Plus, and groundwater were recorded. A control bottle, without PermeOx® Plus, was also constructed and monitored initially.

A second set of bottles was prepared with a 10-fold dilution of the soil and of the groundwater. This set of bottles evaluated what would happen if OBC were used to remove most of the contamination or the treatment was in a more dilute area of the plume and PermeOx® Plus were used to polish the residual constituents. A 120 g aliquot of the soil was amended with 1,080 g of clean sand and thoroughly mixed. Two hundred and twenty mL of groundwater were diluted with 1,980 mL of distilled water. Each of the five bottles received 200 g of the diluted soil and 350 mL of the diluted groundwater. These bottles were amended with 0.7 g of PoxP. A sixth bottle received the 200 g of diluted soil and 350 mL of diluted groundwater, was shaken for one hour, and then sacrificed.

The bottles were allowed to react for up to 3 months at room temperature on a rotary shaker. After 0, 29, 56, 84, and 93 days, the bottles were allowed to settle to produce distinct aqueous and solid fractions. If necessary, the soil and groundwater were transferred to 500 mL centrifuge bottles and centrifuged. The weight of the soil and groundwater fractions was recorded. A 10 mL aliquot of the groundwater was analyzed for pH, ORP, DO, and temperature at each sampling point. The remaining groundwater in that bottle was analyzed for SVOCs at 0, 56, and 93 days. The weight of the groundwater used for each test was recorded. The active oxygen (AO) assay of the PermeOx® Plus remaining in the soil samples was performed at each of the three sampling points. Soil samples were analyzed for SVOCs and PLFA at the beginning and intermediate time point. The weight of the soil samples submitted for SVOC, PFLA, and AO were recorded. If the DO levels drop to below 2 mg/L and little AO remain, additional PermeOx® Plus would be added to the remaining bottles.

The AO assay was conducted as follows. The weight of 250 mL beaker was recorded. Forty-five g of soil was placed into the 250 mL beaker and the weight recorded. The dry weight of soil was determined in a 105 °C oven. The 45 g of soil received 100 mL of 10% phosphoric acid and a magnetic stirrer and was then titrated with 0.5 N potassium permanganate until a light pink color persists for one minute. The volume of potassium permanganate was recorded.

Calculation: % Apparent Active Oxygen = mL permanganate x normality x 0.8/sample weight
% AO = % Apparent Active Oxygen x (1 + soil moisture content)
% PermeOx® Plus = % AO/0.222

Results for Straight Soil. In the straight soil, 7.0 g of PoxP was added to 200 g soil (3.5%) and 351 to 356 mL of groundwater. The initial pH of the soil and groundwater without PermeOx® Plus was 4.2 with an ORP of 270 mV. After incubation for 29 days, the groundwater pH was 11.2 due to the calcium peroxide and the ORP was -91 mV. However, there was 9.6 mg/L of DO - slightly above saturation of 8.8 mg/L at 22 °C. The % apparent active oxygen was 0.483% and there was an estimated 2.94% of PermeOx® Plus. The pH remained elevated above 12 at Day 56 with a DO content of 9.3, again slightly above saturation as the PermeOx® Plus was converted to oxygen. The overall ORP was still negative, - 80 mV. The % apparent active

oxygen and percent PermeOx® Plus declined to 0.424 and 2.68%, respectively. At Day 84, the pH was 11.2, the ORP -104 mV, the DO was 8.4 mg/L, % apparent active oxygen was 0.470, % active oxygen 0.665, and % PermeOx® Plus was 2.99. The pH remained alkaline on Day 93 (11.6), the ORP slightly reducing (-14 mV), but there was 11.4 mg/L of DO, above saturation. The % apparent active oxygen had declined to 0.344, with % active oxygen at 0.476, and % PermeOx® Plus of 2.15. Over the three-month incubation period, about 39% of the PoxP was consumed. The estimated PermeOx® Plus demand was 13.5 g/kg.

The PLFA of the straight soil was measured initially in the Biodegradation Test Control Treatment K. There were 2.08×10^7 cells/g based upon the recovery of PFLA from the soil; this indicates relatively high numbers of microbes. Most of the microbes were Proteobacteria (48.0%) and Firmicutes/anaerobic gram negative (26.2%) with lesser numbers of anaerobic metal reducers (7.4%), sulfate reducing bacteria (SRB) and actinomycetes (4.6%), general bacteria (10.2%), and 3.6% eukaryotes. The ratio of slowed growth was 0.88 and none of the bacteria had decreased permeability. After 29 days, the total biomass declined to 2.19×10^6 cells/g, possibly due to the alkaline conditions. The percentage of firmicutes/anaerobic gram negative, anaerobic metal reducers and SRB/actinomycetes declined as the soil and groundwater became more aerobic. There were decreases in percentages of the Proteobacteria and Eukaryotes. The General bacteria increased to 85%. The ratio of organisms with slowed growth decreased and no bacteria with decreased permeability were found. At Day 93, the biomass increased slightly to 6.66×10^6 cells/g. The percent of the population that were proteobacteria increased and the number of general bacteria decreased. No organisms with slowed growth or decreased permeability were detected. Some microbial inhibition occurred.

Over the 93 day incubation period of the straight soils, there were large decreases of more than 50% in the soil concentrations of 4-nitrophenol, PCP, naphthalene, 2-methylnaphthalene, acenaphthylene, acenaphthene, dibenzofuran, fluorene, n-nitrosodiphenylamine, phenanthrene, anthracene, carbazole, fluoranthene, pyrene, benzo(a)anthracene, chrysene, benzo(b)fluoranthene, benzo(a)pyrene, indeno(1,2,3-cd)pyrene, and benzo(g,h,i)perylene with a smaller decline only in benzo(k)fluoranthene. Total SVOCs in the soil phase decreased by 70%. Similar decreases were noted for the phenols and PAHs in the aqueous phase. Reductions of more than 50% were noted for the following compounds in the aqueous phase: 2-methylphenol, 4-methylphenol, 2,4-dimethylphenol, PCP, naphthalene, 2-methylnaphthalene, acenaphthylene, acenaphthene, dibenzofuran, fluorene, phenanthrene, fluoranthene, and pyrene. Total SVOCs decreased by 71% in the aqueous phase.

Results for Diluted Soil. For the diluted soil samples, 0.7 g of PoxP was added to 200 g soil (0.35%) and 351 to 352 mL of groundwater. The initial pH of the diluted soil and groundwater without PermeOx® Plus was 4.5. The initial ORP was 290 mV. The groundwater pH was 10.2 due to the calcium peroxide after incubation for 29 days. The ORP was -60 mV. There was 9.3 mg/L of DO - slightly above saturation of 8.8 mg/L at 22 °C. The % apparent active oxygen was 0.019% with an estimated 0.10% of PermeOx® Plus. An elevated pH (10.6) was found at Day 56 with a DO content of 9.0, again slightly above saturation as the PermeOx® Plus was converted to oxygen. The overall ORP was still negative, - 78 mV. The % apparent active oxygen and percent PermeOx® Plus declined to 0.012 and 0.064%, respectively. Similar results were observed on Days 84 and 93 with pH of 9.0-9.8, DO of 6.4-7.0, ORP of -30 to 46 mV, %

apparent active oxygen of 0.0068 to 0.0080, and % PermeOx® Plus of 0.036 to 0.043. About 90% of the PermeOx® Plus was consumed in 93 days. The estimated PermeOx® Plus demand for the diluted soil was 3.2 g/kg.

The PLFA of the diluted soil was measured initially indicated 1.85×10^7 cells/g based upon the recovery of PFLA from the soil; this indicates relatively high numbers of microbes. Most of the microbes were Proteobacteria (39.4%) and Firmicutes/anaerobic gram negative (34.0%) with lesser numbers of anaerobic metal reducers (8.9%), sulfate reducing bacteria (SRB) and actinomycetes (4.4%), general bacteria (10.4%), and 2.9% eukaryotes. The ratio of slowed growth was 0.48 and none of the bacteria had decreased permeability. The total biomass declined to 6.63×10^6 cells/g, possibly due to the alkaline conditions. The percentage of firmicutes/anaerobic gram negative, anaerobic metal reducers and SRB/actinomycetes declined as the soil and groundwater became more aerobic. There were decreases in percentages of the Proteobacteria and Eukaryotes. The general bacteria increased to 65.7%. The ratio of organisms with slowed growth increased to 1.94 and no bacteria with decreased permeability were found. At Day 93, the total biomass increased to 2.98×10^7 cells/g; slightly above the initial level. The percent firmicutes continued to decline with a large increase in the percent of population that were proteobacteria and fewer general bacteria. No bacteria with slowed growth or decreased permeability were found at Day 93. The addition of the PermeOx® Plus, and the oxygen it produced, resulted in a higher biomass.

There were large decreases of more than 50% over the 93 day incubation period in the diluted soil concentrations of PCP, naphthalene, 2-methylnaphthalene, acenaphthylene, acenaphthene, dibenzofuran, fluorene, n-nitrosodiphenylamine, phenanthrene, anthracene, carbazole, fluoranthene, pyrene, benzo(a)anthracene, chrysene, benzo(b)fluoranthene, and benzo(a)pyrene. A smaller decline was noted for benzo(k)fluoranthene and indeno(1,2,3-c)pyrene, dibenz(a,h)anthracene, and benzo(g,h,i)perylene were detected at days 56 and 93, but in the initial samples. Total SVOCs decreased by 78% in the soil phase.

In the aqueous phase over the 93 day incubation period, the following compounds were reduced by >50%: 2,4-dimethylphenol, PCP, naphthalene, 2-methylnaphthalene, acenaphthylene, acenaphthene, dibenzofuran, fluorene, phenanthrene, and carbazole. Less extensive removals were seen for anthracene, benzo(a)anthracene, chrysene, and benzo(a)pyrene. In the aqueous phase of the diluted soils, biological degradation resulted in an 83% reduction in the concentrations of the SVOCs.

CONCLUSIONS

- The total oxidant demand for OBC to treat the highly contaminated soils was found to be between 6.9 g/kg to 11.1 g/kg or 18.7 to 30 pounds per cubic yard
- Additional base equivalent beyond the alkalinity available from the OBC was necessary to maintain the alkaline pH conditions for activation of the sodium persulfate
- The OBC persisted in the microcosms for at least two months
- Over the 64 days of treatment with OBC over 23% of the SVOCs in the soil phase were destroyed and 40% of the SVOCs in the aqueous phase
- The estimated OBC oxidant demand over the 64-day incubation period was 15.3 g/kg.

- The PermeOx® Plus resulted in the aerobic biodegradation of SVOCs in the soil phase by least 70% and in the aqueous phases by 71% over three months of treatment. The PermeOx® Plus demand for the straight soil was estimated to be 13.5 g/kg.
- In the diluted soil treated with PermeOx® Plus to simulate pretreatment with OBC or treatment of a less contaminated area, the SVOC concentrations in the soil phase declined by 76% and by 83% in the aqueous phase. The PermeOx® Plus demand for the diluted soil was 3.2 g/kg.
- The combination of OBC to reduce the contaminant mass and PermeOx® Plus to polish the remaining contaminants was found to be promising.

Despite significant chemical loading required by the highly contaminated soil and groundwater, only a temporary one-log depression in overall viable biomass was observed and in all cases the microbial population rebounded with an advantageous shift in the specific types of microorganisms (e.g., proteobacteria).

The treatability study consisting of de-coupled chemical oxidation and enhanced biodegradation experiments was effective in showing efficacy and the project team elected to move aggressively into pilot testing including a one year performance monitoring period. Design basis information for the pilot test was successfully extracted from the treatability study. Relatively high loading of OBC with additional alkalinity became the basis for pursuing significant CoC removal at WC-5 and WC-23 via base activated persulfate chemical oxidation followed by enhanced aerobic biodegradation. Where enhanced bioremediation alone is indicated, PermeOx® Plus was deemed to be effective but again significant loading was found to be necessary where soil impact is relatively high. A decision was made to test this approach at the WC-40 hot spot.

The pilot test design turned out to be similar to the conceptual coupled Chem-Bio design presented previously in Figure 3 with a significant difference being the initial step of injecting PermeOx Plus slurry to pre-condition the planned OBC application area by increasing the pH and raising the DO. Once PermeOx® Plus was emplaced then OBC was injected. This tactic was pursued to achieve a sustained elevated pH leading to In Situ NOM Extraction™ resulting in CoC mass transfer to the aqueous phase, more persulfate anion conversion to radical state and ultimately enhanced probability of broader reactions, more rapid destruction, and more mass destruction. The additional PermeOx® Plus would then evolve more DO over a longer period of time to support expected aerobic bioactivity once chemical oxidation reactions subsided. At the point that the property owner decides to not add more oxygen, then the pilot test areas would each convert back to anaerobic conditions and some anoxic oxidative reactions (e.g., involving utilization of the added sulfate via SRB) could be expected to provide additional benefit – the significance of which can not be determined *a priori* but through long term monitoring much might be learned.

A one-year duration pilot test involving the three areas of concern was started May 2007 with the baseline sampling of groundwater. Two chemical injection rounds have been completed. The first round occurred in May 2007 and involved the application of 11,754 lbs PermeOx® Plus and 10,186 lbs OBC at an average slurry weight of approximately 24%w/w. The second injection round occurred in November 2007 and involved application of 2556 lbs PermeOx® Plus and 7700 lbs OBC at slurry weights of 21% and 22%/w/w, respectively. Performance monitoring

started after the first injection round and groundwater sampling and analysis data, including field geochemical parameter data, have been developed for two dates prior to the second injection round.

Preliminary field observations including laboratory analytical results indicate that pH above 10 s.u. was achieved and sustained at WC-5 and WC-23. DOC increased significantly at WC-23 and less so at WC-5. ORP and DO levels were significantly elevated and significant CoC concentration reductions were measured, in some cases 50% or more from baseline concentrations. Persulfate anions (>70 ppm using field test kit) have been detected five months after application. Only PermeOx Plus was injected up gradient of WC-40 during the first round and less geochemical impact was observed. Due to groundwater flow direction and rate uncertainty, it is speculated that WC-40 is not positioned for optimal observation of geochemical changes and the effects of enhanced bioactivity on CoC concentrations.

If significant contaminant reductions are observed during the pilot test period as a result of chemical oxidation and subsequent aerobic bioremediation, then additional limited treatment may be pursued. Once active treatment is terminated the project team expects that anaerobic conditions will re-establish. It is speculated that information on the nature of that future transition and whether the active treatments ultimately detract from or contribute to (as they are expected to do) subsequent natural attenuation processes will require at least several additional years of groundwater monitoring.

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