INNOVATIVE PROTOCOLS FOR IN SITU MTBE DEGRADATION BY USING MOLECULAR PROBES-AN ENHANCED CHEMICAL-BIO OXIDATION TECHNIQUE

TOPICAL REPORT

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DISCLAIMER

ABSTRACT

In situ chemical oxidation (ISCO) is a common technology to cleanup petroleum hydrocarbon-contaminated soils and groundwater. Sodium percarbonate (SPC) is an oxidant which is activated by iron (Fe) to produce Fenton-like reactions. Western Research Institute, in conjunction with Regenesis and the U.S. Department of Energy, conducted a study that investigated the performance of a "safe" oxidant, SPC, to cleanup groundwater and soils contaminated with petroleum hydrocarbons and associated contaminants (e.g., MTBE). Results from a field pilot test in Frenchglen, Oregon showed VOC concentrations in groundwater decreased substantially within 2 weeks after injecting activated SPC (RegenOx). A protocol was established for determining RegenOx TOD in soils and groundwater. Total oxidant demand tests were necessary to determine the correct dosage of RegenOx to apply in the field and sufficiently degrade the contaminants of concern. Bench studies with RegenOx showed this technology was effective in degrading diesel fuel and 1,4-dioxane. The Fe-silica activator (RegenOx Part B) was tested with another oxidant, sodium persulfate. Bench tests results showed the combination of sodium persulfate and RegenOx Part B was effective in reducing PCE, MTBE, benzene, and n-heptane concentrations in water. Overall, the results of this project indicated that most petroleum contaminants in soil and groundwater can be sufficiently degraded using the RegenOx technology.

EXECUTIVE SUMMARY

Current petroleum operations produce about 930 billion gallons of crude oil worldwide per year. Handling of such large amounts of petroleum products often results in contamination of soils. Leaking underground storage tanks (LUST) have been a continuing major contributor to soil and groundwater contamination. In situ chemical oxidation (ISCO) is a common method of removing organic contaminants from soils and groundwater. Hydrogen peroxide (H_2O_2) has been extensively studied as a chemical reagent to remove petroleum contaminants from soils, often associated with Fenton or Fenton-like reactions. Fenton reactions utilizes Fe^{2+} to catalyze decomposition of H_2O_2, producing a much more powerful oxidizer in the form of OH radicals. It has been reported that surface sites soil minerals and oxides in the presence of H_2O_2 may produce Fenton-like reactions. Sodium percarbonate (SPC) is a cheap, mass-produced solid peroxygen compound that has been mainly used as sources of H_2O_2 for stain bleaching. SPC is easily stored with minimal handling hazards, having no shock sensitivity, and is non-toxic, presenting no environmental hazard; however, relatively little studies have been done on SPC's ability to oxidize petroleum contaminants. In past remediation applications, SPC has been used as a oxygen releasing material to stimulate microbial activity, thus enhancing biodegradation of organic contaminants. However, in the presence of a suitable catalyst, H_2O_2 liberated from SPC can be utilized in contaminant oxidation in soils and groundwater systems. Due to its relative lack of handling hazards, non-toxicity to the environment, low cost and availability, SPC is potentially a viable oxidant for remediating petroleum contaminated soils and groundwater.

The original proposed work for Task 52 was to develop a protocol for *in situ* treatment of MTBE in groundwater using PM1 molecular probe to identify the presence and enumerate MTBE-degrading bacteria in the groundwater. If necessary, PM1 will be amended to the MTBE plume along with a proprietary oxidation process, which is designed to create an aerobic environment to achieve the degradation. The objective of this proposed work was modified to evaluate the efficiency of SPC in degrading petroleum contaminants (including MTBE) and develop a standard protocol to determine total oxidant demand (TOD) to improve *in-situ* chemical oxidation (ISCO) applications using SPC. The SPC used in this project was provided by Regenesis under the proprietary label RegenOx. The SPC in RegenOx is activated by a Fe-silica mixture (RegenOx Part B) to create a Fenton-like reaction.

Western Research Institute in conjunction with Regenesis and the U.S. Department of Energy conducted a study that investigated the performance of a "safe" oxidant, SPC, to cleanup groundwater and soils contaminated with petroleum hydrocarbons and associated contaminants (e.g., MTBE). The results of this study are summarized as follows:

- Results from a field pilot test in Frenchglen, OR, showed VOC concentrations in groundwater decreased substantially within 2 weeks after injecting activated SPC (RegenOx). However, concentrations rebounded due to the consumption of the oxidant and the plume movement.

- A protocol was established for determining RegenOx TOD in soils and groundwater. Total oxidant demand tests were necessary to determine the correct dosage of RegenOx to apply in the field and sufficiently degrade the contaminants of concern. Tests were performed to validate the TOD method where soils contaminated with diesel fuel and PAHs were used. Results of these tests also indicated little to no mobilization of metals occurring with an overdosed of RegenOx.

- Bench studies with RegenOx showed this technology was effective in degrading diesel fuel and 1, 4-dioxane. However, the results for individual PAHs are inconclusive.

- The Fe-silica activator (RegenOx Part B) was tested with another oxidant, sodium persulfate. Bench tests results showed the combination of sodium persulfate and RegenOx Part B was effective in reducing PCE, MTBE, benzene, and n-heptane concentrations in water.

Overall, the results of this project indicated that most petroleum contaminants in soil and groundwater can be sufficiently degraded using the RegenOx technology. Also, an important TOD protocol was established to maximize the performance of RegenOx in field applications.

INTRODUCTION

Current petroleum operations produce about 930 billion gallons of crude oil worldwide per year. Handling of such large amounts of petroleum products often results in contamination of soils. Leaking underground storage tanks (LUST) have been a continuing major contributor to soil and groundwater contamination. In the United States alone, there are more than 250, 000 LUST resulting in the contamination of soils and groundwater. Gasoline range organic (GRO) compounds, which include volatile organic compounds (VOC), can be persistent in subsurface environments when inadequate amounts of nutrients and oxygen are present for natural attenuation.

Chemical oxidation is a common method of removing organic matter from soils for analyses of the mineral phase, which include particle size distribution, soil composition, and cation exchange capacity. In theory, the end products of chemical oxidation are CO_2 and H_2O. Organic matter removal by chemical oxidation is controlled by reaction conditions, such as pH, contact time, and chemical additives, and soil properties (Mikutta et al., 2005). Additionally, organic matter may not be completely be removed by chemical oxidation, which may be due to soil reaction, presence of carbonates, resistant organic compounds, and interference by mineral surfaces (Mikutta et al., 2005). Despite these limitations, studies have been done to improve organic removal by chemical oxidation.

Chemical oxidation studies have been done with hydrogen peroxide (H_2O_2), sodium hypochlorite (NaOCl), and disodium peroxodisulfate ($Na_2S_2O_8$). H_2O_2 has been extensively studied as a chemical reagent to remove petroleum contaminants from soils, often associated with Fenton or Fenton-like reactions (Kanel et al., 2003; Greenberg et al., 1998; Sedlak and Andren, 1991a, 1991b; Vitolins et al., 2003; Watts et al., 2002; Xie an Barcelona, 2003). Fenton reactions utilizes Fe^{2+} to catalyze decomposition of H_2O_2, producing a much more powerful oxidizer in the form of OH radicals. It has been reported that surface sites soil minerals and oxides in the presence of H_2O_2 may produce Fenton-like reactions (Huang et al., 2001; Gournis et al., 2002; Kwan and Voelker, 2002; Petigara et al., 2002). Fenton-like chemistry can be represented as,

$$--M^{2+} + H_2O_2 \rightarrow --M^{3+} + {^\cdot}OH + OH^-$$
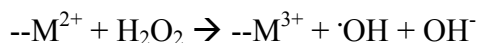
OH radicals have been reported to decompose organic compounds with aromatic structures at higher rates than organic compounds with aliphatic structures (Xie and Barcelona, 2003).

Sodium percarbonate (SPC) is a cheap, mass-produced solid peroxygen compound that has been mainly used as sources of H_2O_2 for stain bleaching. SPC is easily stored with minimal handling hazards, having no shock sensitivity, and is non-toxic, presenting no environmental hazard (McKillop and Sanderson, 1995). The name "sodium percarbonate" does not represent the true structure and nature of the material, which is also called sodium carbonate

sesquiperhydrate, $2Na_2CO_3 \cdot 3H_2O_2$. The alkaline compound shows H_2O_2 to be loosely bound and is readily displaced by moisture, disrupting the crystal structure (Carrondo et al., 1977; McKillop and Sanderson, 1995). SPC chemistry in aqueous solution is similar to alkaline H_2O_2 chemistry (Kabalka et al., 1990), and SPC reactivity may be enhanced by true percarbonate formation. In solution, H_2O_2 is liberated and the perhydroxyl ion is formed,

$$H_2O_2 \longleftrightarrow H^+ + HO_2^-$$
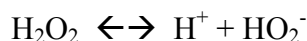
Percarbonate, CHO_4^-, formation may be attributed to CO_2 action (Jones and Griffith, 1980),

$$HO_2^- + CO_2 \rightarrow HCO_4^-$$
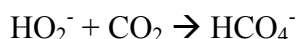
or it is formed in equilibrium (Flanagan et al., 1986),

$$HCO_3^- + H_2O_2 \longleftrightarrow HCO_4^- + H_2O$$
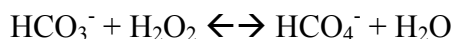
In non-aqueous systems, SPC can be a direct source of H_2O_2 (McKillop and Sanderson, 1995), and the liberation of H_2O_2 can be achieved at an adequate rate (Rocha Gonsalves et al., 1991).

Relatively little studies have been done on SPC's ability to oxidize petroleum contaminants. In past remediation applications, SPC has been used as an oxygen releasing material to stimulate microbial activity, thus enhancing biodegradation of organic contaminants (Vesper et al., 1994). However, in the presence of a suitable catalyst, H_2O_2 liberated from SPC can be utilized in contaminant oxidation in soils and groundwater systems. Due to its relative lack of handling hazards, non-toxicity to the environment, low cost and availability, SPC is potentially a viable oxidant for remediating petroleum contaminated soils and groundwater.

The original proposed work for Task 52 was to develop a protocol for *in situ* treatment of MTBE in groundwater using PM1 molecular probe to identify the presence and enumerate MTBE-degrading bacteria in the groundwater. If necessary, PM1 will be amended to the MTBE plume along with a proprietary oxidation process, which is designed to create an aerobic environment to achieve the degradation. The objective of this proposed work was modified to evaluate the efficiency of SPC in degrading petroleum contaminants (including MTBE) and develop a standard protocol to determine total oxidant demand (TOD) to improve *in situ* chemical oxidation (ISCO) applications using SPC. The SPC used in this project was provided by Regenesis under the proprietary label RegenOx. The SPC in RegenOx is activated by a Fe-silica mixture (RegenOx Part B) to create a Fenton-like reaction.

RESULTS

Performance of ISCO using Sodium Percarbonate: Field Study

The Frenchglen project was a pilot study to gain an understanding of ISCO of contaminants in groundwater. The study consisted of three phases: (1) baseline groundwater monitoring, (2) *in situ* chemical oxidation injection, and (3) post injection groundwater monitoring and analysis.

Activated SPC (RegenOx) was applied at the site through direct injection. Groundwater samples were collected from monitoring wells (MW14 and MW15) at a site. Pre- and post-treatment samples were obtained to evaluate the remedial efficiency. Parameters were analyzed by using the methods listed in Table 1.

Table 1. Parameter and Methods List for Groundwater Collected at the Frenchglen Site

Parameter	Method
VOC	8260
GRO	GC-MS
Bicarbonate/Carbonate Alkalinity	HACH
C1, NO_3, SO_4	IC
Sulfide	Colorimetric 376.2
Na, Ca, Mg, K	AA
Cr, Cr^{6+}, Fe, Mn, (total and dissolved)	ICP-MS

Figures 1-4 summarize the effectiveness of the RegenOx in the field pilot study. Overall reduction of volatile organic compounds (VOCs) was observed for most constituents upon the completion of field injection, indicating the RegenOx was effective in destruct petroleum hydrocarbons. The bounce-back of some constituents may be attributed to desorption of these compounds from the soil or sediments and the plume moving with groundwater flow.

Figures 5 and 6 depict the trends of chromium (Cr) and common cations (Ca, Mg, K) over time. Concentrations of Cr and the cations decreased substantially after the injection of RegenOx, which appears to be effective in metal immobilization. This technology may be applicable to address co-mingled contaminants of petroleum hydrocarbons and metals in groundwater.

Figure 1. 1,2-Dichloromethane Concentrations in Groundwater After Injection of RegenOx

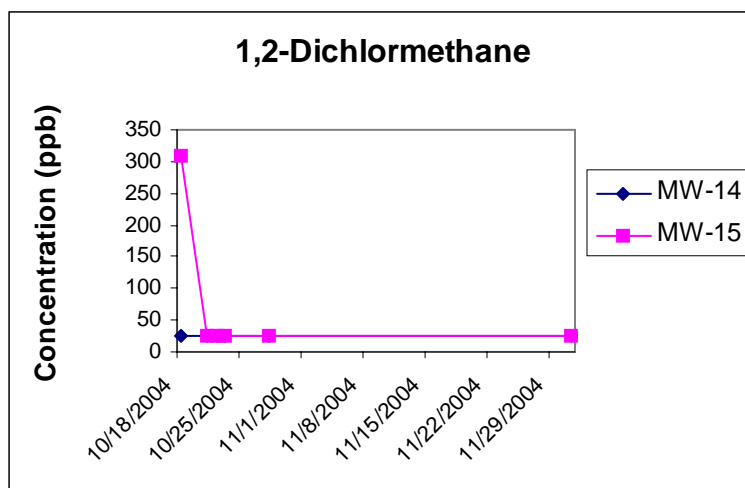**Figure 2. Isopropylbenzene Concentrations in Groundwater After Injection of RegenOx**
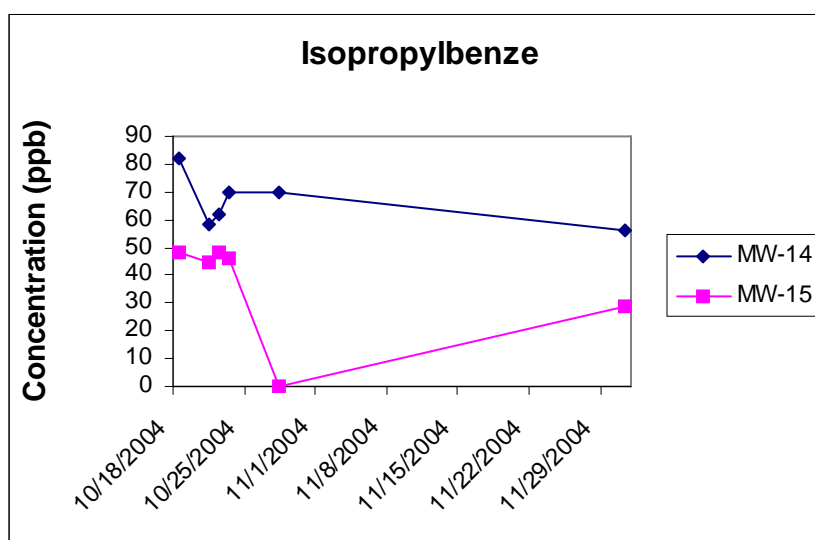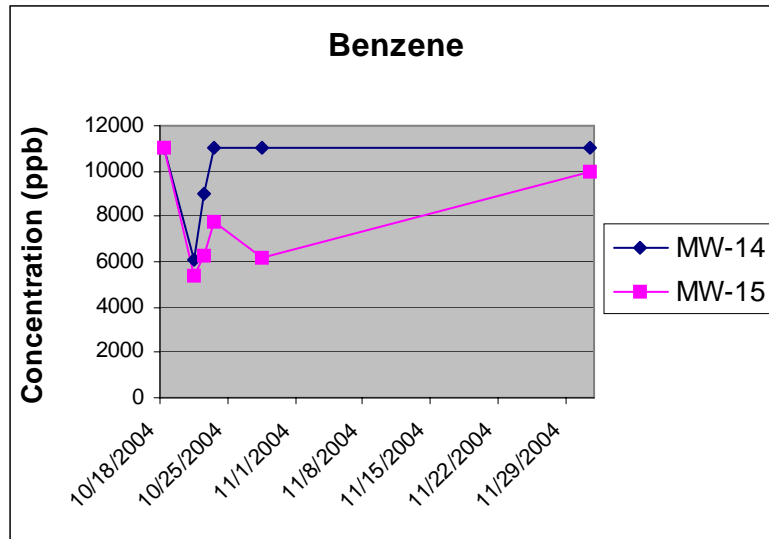
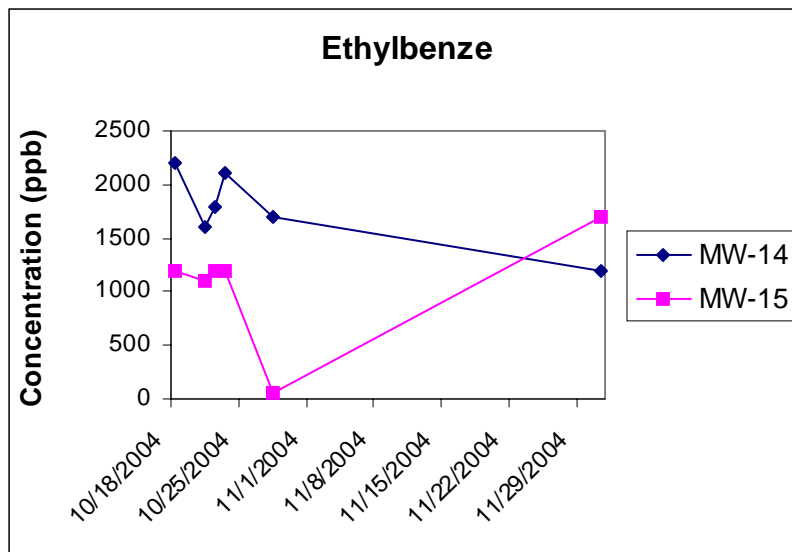**Figure 3. Benzene Concentrations in Groundwater After Injection of RegenOx**

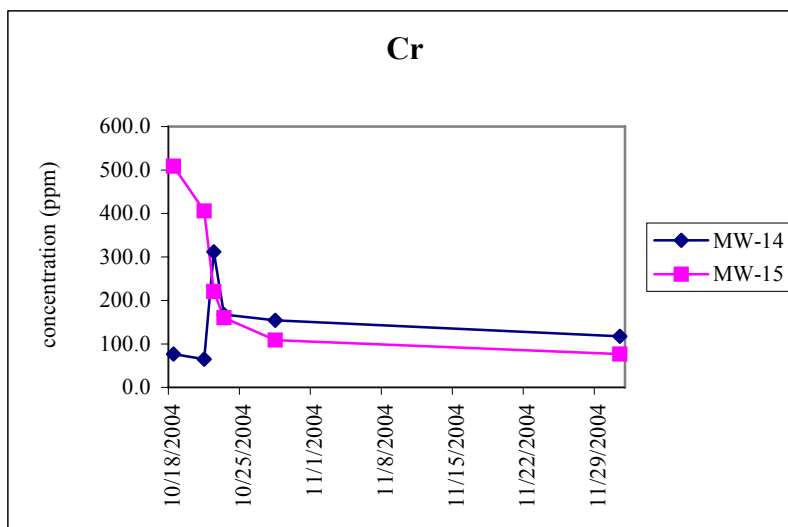**Figure 4. Ethylbenzene Concentrations in Groundwater After Injection of RegenOx**

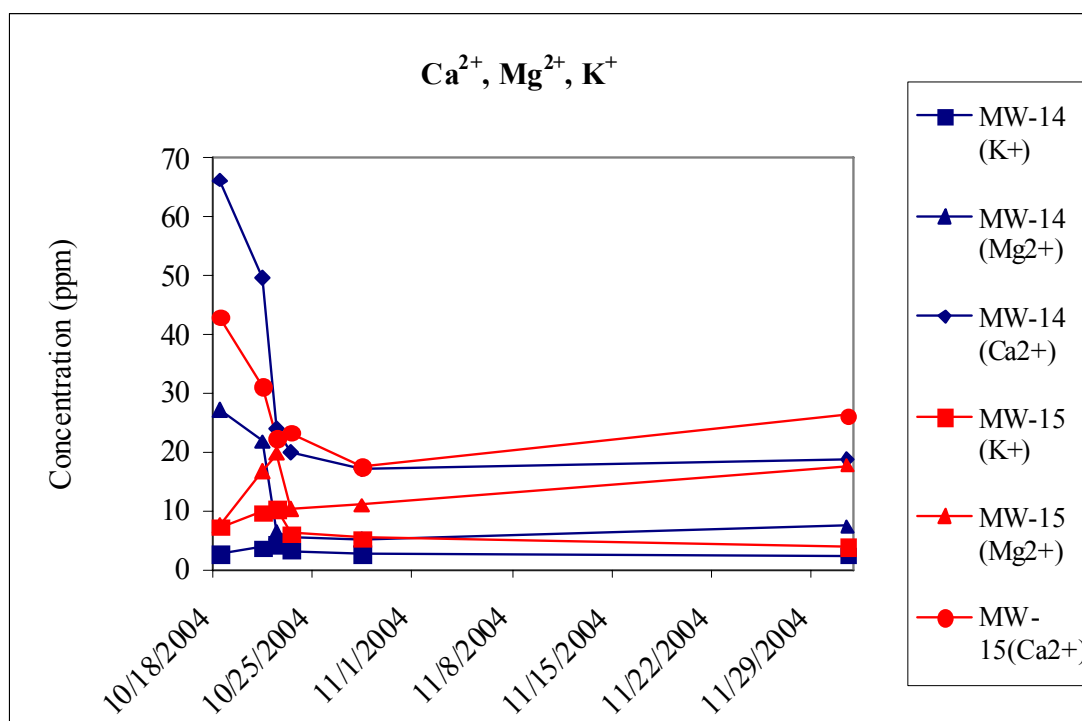**Figure 5. Chromium Concentrations in Groundwater After Injection of RegenOx.**

Figure 6.Common Cation Concentrations in Groundwater After Injection of RegenOx

Groundwater samples were collected from monitoring wells (MW13, MW15 and TEMP) at a pilot study site in Montgomery, Alabama. Parameters were analyzed using the methods listed in Table 2. Analytical results are summarized in the Table 3.

Table 2.   Parameters and Methods for Analysis of Groundwater at the Montgomery Site.

Parameter	Method
Bicarbonate/Carbonate Alkalinity	HACH
C1, NO_3, SO_4	IC

Table 3.   Analytical Data Summary for Samples Collected at the Montgomery Site.

Sample ID	Date Sampled	Bicarbonate Alkalinity (mg/L)	Carbonate Alkalinity (mg/L)	Cl (mg/L)	NO_3 (mg/L)	SO_4 (mg/L)
MW-3	6/20/2005	80	0	14.183	N.D.	11.453
MW-5	6/20/2005	40	0	16.286	N.D.	5.271
TEMP	6/20/2005	40	0	17.186	N.D.	10.679

Total Oxidant Demand Protocol and Tests

A protocol was established for total oxidant demand (TOD) where activated SPC (RegenOx) is the oxidant. This involved (1) evaluating the use of a control sample to understand the effects of the soil on a given sample's absorbance (2) analyzing the full spectrum (190-1100 nm) for a wavelength less susceptible to other constituents other than percarbonate, and (3) determining the lower limit of detection for the method. These tests were deemed necessary as TOD is the key parameter in the application of this controlled oxidation process. Inaccurate readings could lead to over or under dosing a given site.

By analyzing a control sample, it was found that absorbance readings could be influenced from 0.007-0.060 and was soil dependent. Analyzing samples of different concentrations of percarbonate across the full spectrum revealed that the predetermined wavelength was most effective in determining SPC and that no suitable substitute could be confidently used. Therefore, the use of a control sample to remove unrelated influences from the absorbance reading was amended into the initial protocol. In some cases, removing these influences made a significant difference in the dosage applied at an impacted site. TOD analyses continued as new samples were received using the updated protocol. These analyses will be used in building a database used to compare soil characteristics to TOD.

A larger scale, comprehensive test was also performed on two impacted Alaskan soils. This was accomplished to determine the feasibility of using RegenOx technology in remediating hydrocarbon-contaminated soils in cold climates. This test was performed by mixing 3L of site water to 300g soil. A control batch, which received no treatment, was created to compare to a treated batch, which received 30,000 ppm RegenOx. These mixtures were then held for 72h at 8°C. Samples for total petroleum hydrocarbons (TPH) in the soil and water were taken before the treatment was added and after 72h. The results from these tests are listed in Table 4.

Samples for TOD were taken from the treated batch at specified times during the 72h. Results from the comprehensive tests indicate that the use of RegenOx technology is effective in reducing TPH in the soil and that the TOD was met at the prescribed dosage of 30,000 ppm across 72 hours under in a cold environment (Figure 7). However, an increase in TPH in the water suggests contaminants may only be leached from soil. Further investigation is necessary to determine if hydrocarbons are being broken down into different chain-length compounds or completely oxidized. This will give a better understanding to the actual effectiveness of the technology.

Table 4.Total Petroleum Hydrocarbon (TPH) Concentrations in Soils for TOD Tests

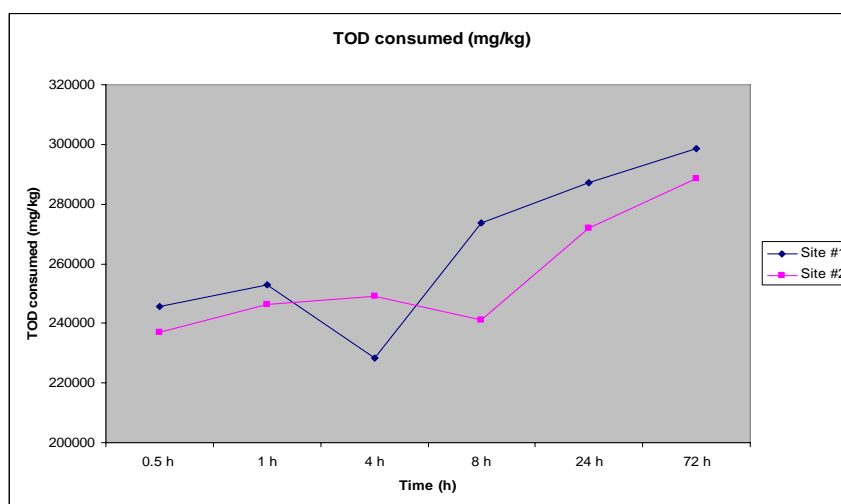| Sample ID	TPH (mg TPH/kg - soil) or (mg TPH/L - water)			
	Initial Soil	Initial Water	Final (72 h) Soil	Final (72 h) Water
Site #1 Control	2900	1.0	4200	0
Site #1 Treated (30,000 ppm RegenOx)	2900	1.0	1800	1.4
Site #2 Control	80750	0	60700	8.8
Site #2 Treated (30,000 ppm RegenOx)	80750	0	6500	15.2

Figure 7. TOD (Consumed) for the Treated Batches of Alaskan Soils

RegenOx was tested on two hydrocarbon-impacted soils (ASA and A-711). Results from the ASA soil test indicate: (1) an application of the activator (Part B of RegenOx) at 30,000 ppm is effective in reducing TPH by 46% and DRO by 70% within 72 hours; (2) an application of the activator and oxidant (Part A and B) at 30,000 ppm effectively reduces TPH by 33% and DRO by 91%; and (3) the application of either activator alone or in combination with oxidant results in increased metal mobilization, especially arsenic (As), barium (Ba), chromium (Cr), and lead (Pb). Moderate mobilization was also noted in selenium (Se), silver (Ag) and mercury (Hg).

Results from the A-711 soil test demonstrate: (1) an application of the activator at 30,000 ppm is effective in reducing overall TPH by 79%, DRO by 64% , and RRO by 60% within 72 hours; (2) an application of the activator and oxidant at 30,000 ppm effectively reduces TPH by 90%, DRO by 88%, and RRO by 86%; (3) the application of either activator alone or in combination with oxidant results in increased metal mobilization, especially As, Ba, Cr, Pb, and Se. Moderate mobilization was also noted in Se, Ag, and Hg. A decrease in cadmium (Cd) was noted between the controls and the samples containing activator alone or in combination with oxidant; (4) PAH concentration was reduced by the addition of activator only from 62% (benzo[k]fluoranthene) to 80% (naphthalene); and (5) PAH concentration was reduced by the addition of activator and oxidant from 88% (benzo[b]fluoranthene) to 95% (benzo[k]fluoranthene) (Figure 8).
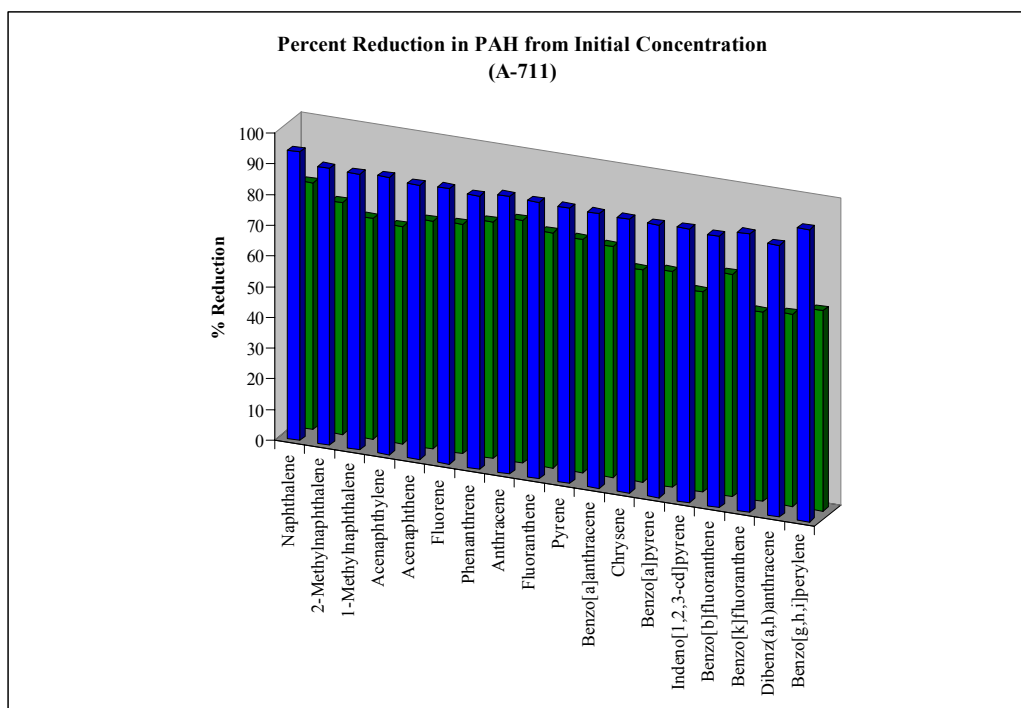

Figure 8. Percent Reduction in PAH Concentration in Activator Only Batch (green) and Activator and Oxidant Combined (blue)

Results from both soil tests indicate the RegenOx is an effective tool in reducing hydrocarbon at 8°C at a dosage of 30,000 ppm during the 72 hr reaction. It is likely that a greater reduction would have occurred had the samples been allowed to react for a longer time. TOD readings are consistent with the reduction of contaminants. Higher TOD indicates more reduction of contaminants, as shown in the TOD data (Figure 9). The results of these tests helped finalize the TOD protocol which is attached to this report in Appendix A.

**TOD Consumed (mg RegenOx/kg soil)
at 300,000 mg/kg dosage**
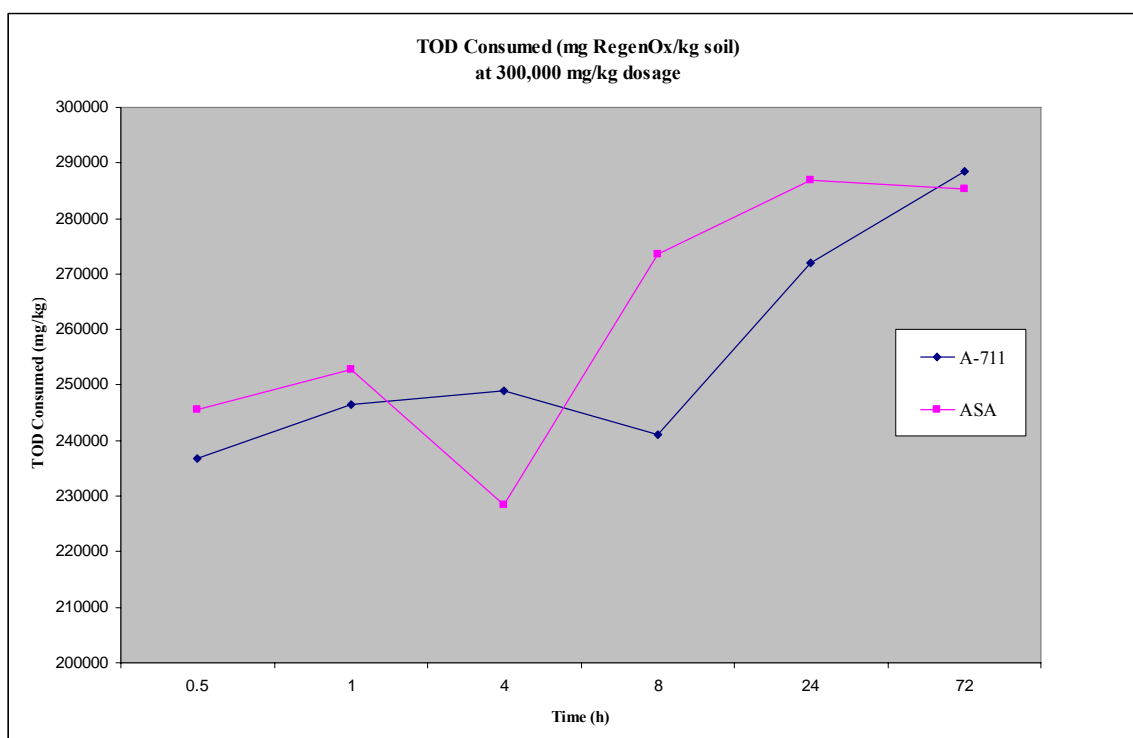
Figure 9. TOD Results as mg RegenOx Consumed Per kg Soil

Bench Tests: Chemical Oxidation of Different Contaminants

1,4-Dioxane

The effect of RegenOx on the degradation of 1,4-dioxane was investigated involving two tests, in which the concentration of RegenOx applied was held constant, but the time allowed for subsequent reactions to take place was varied from 24 hours to 48 hours. Results from this test are shown in Figure 10. Unlike previous tests, a TOD screening was used to determine the point at which the maximum amount of degradation had occurred. This was done by comparing the 24 hour TOD readings to the 48 hour readings for SPC, using the established protocol. Results from these tests are shown in Figure 11. The optimal point was determined at either the near depletion of SPC or when consumption had ceased (SPC consumption plateaus). This method was deemed appropriate based on the results of the test and was incorporated into the TOD protocol for bench tests.

Figure 10. Degradation of 1,4-Dioxane Analyzed by GC-MS at 24 Hours and 48 Hours.(Controls are denoted as (●) for the 24 hour test and (▼) for the 48 hour test. Treated samples are shown as (○) for the 24 hour test and (△) for the 48 hour test)

Figure 11. TOD Results Used to Determine the Point of Maximum Degradation of 1,4 Dioxane (Results from the 24 hour test are shown as (●) and from the 48 hour test as (○))

Diesel and PAHs

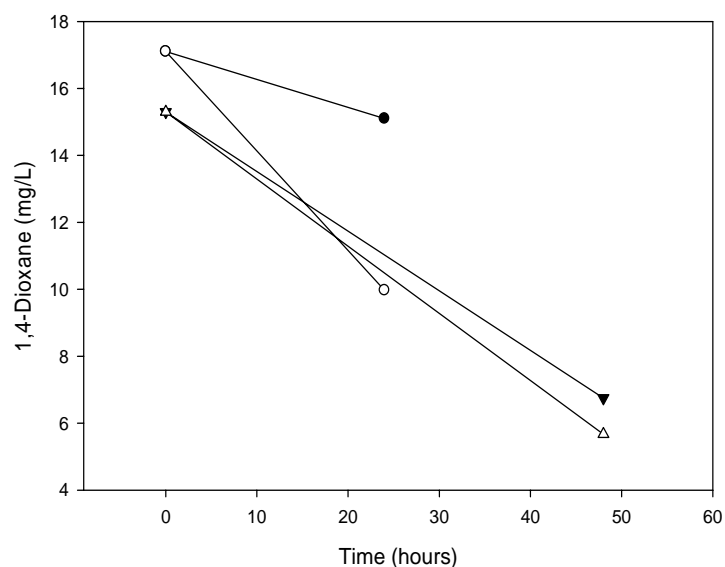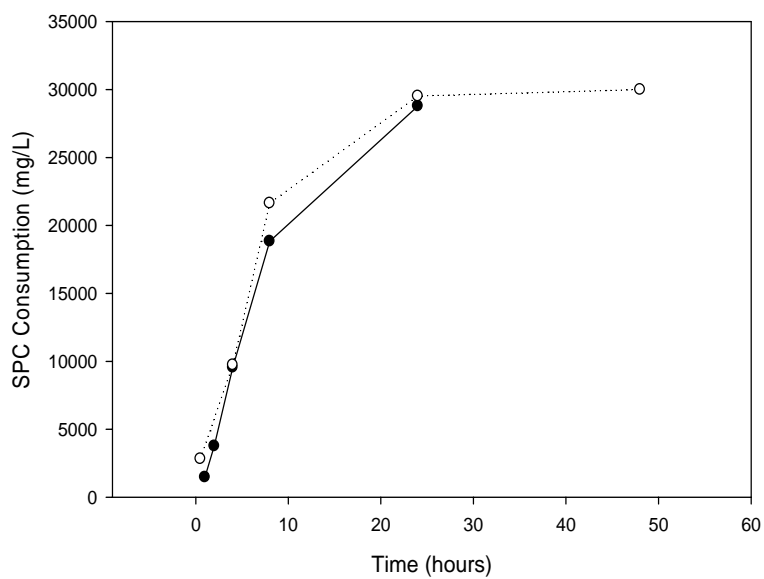A minimum of 1.5 kg of a contaminated site soil and 1 L of site groundwater are typically collected from a desired representative area of the field site and sent to Western Research Institute (WRI) in Laramie, WY. Upon receipt of the samples at WRI, the samples are homogenized for uniformity, placed in air-tight containers, sealed and kept at 4°C until assembly of the bench-scale test.

Triplicate reactors were established using site soil and site water previously collected. Two mandatory sets included in the test are a control set and a treated set. The control set could include the introduction of another oxidant, such as hydrogen peroxide (H_2O_2), adjusting the pH, or both. The basic assembly was identical for both sets and any other sets desired for the test. This involved placing either 30 g of site soil and 300 mL of site water into a 500-mL brown-glass jar, or 10g of site soil with 100 mL site water into a 300-mL brown-glass jar, depending on the desired analyses. The jars were then either kept covered or capped in order to prevent evaporation.

Prior to the application of oxidant, both sets are mixed for 24 h with a stirring bar. At time 24 h, the sets are taken off the stirrer, and allowed to settle for 1 h. At that point, the sets are sampled for any initial or background reading and the oxidant is added. For the analysis of diesel and Cr(VI), RegenOx was added at a concentration of 1,000 mg/L (oxidant and activator). For the coal tars of high concentrations of diesel, the oxidant was added at 5,000 mg/L and the activator at 15,000 mg/L. Tests performed in the past by Regenesis have shown that these concentrations and ratios of oxidant to activator have been the most effective for the application.

The first test of the effect of RegenOx on diesel was performed using three sets of samples: Control (No Activator), Control (Activator Only), and Activator and Oxidant. Treatment was set up as a two fold application. The first application contained 5,000 mg/L oxidant and 15,000 mg/L activator followed by a second application at 24 h of the same amounts. Samples were taken prior to the second application and also 24 h following the second application.

As shown in Figure 12, RegenOx was highly effective at degrading the diesel in the tested samples (~88%) after the 24 h sampling point. The test also found that the activator effectively increased the availability of the diesel, which provided for modest degradation without the presence of the oxidant.

A separate test was performed to see the effect of pH on the breakdown of diesel. This was done by lowering the pH of treated samples from ~11.0 to 7.0 and allowed to react for 72 h. A baseline of the soil was also performed for comparison. The results from this test are shown in Table 5.
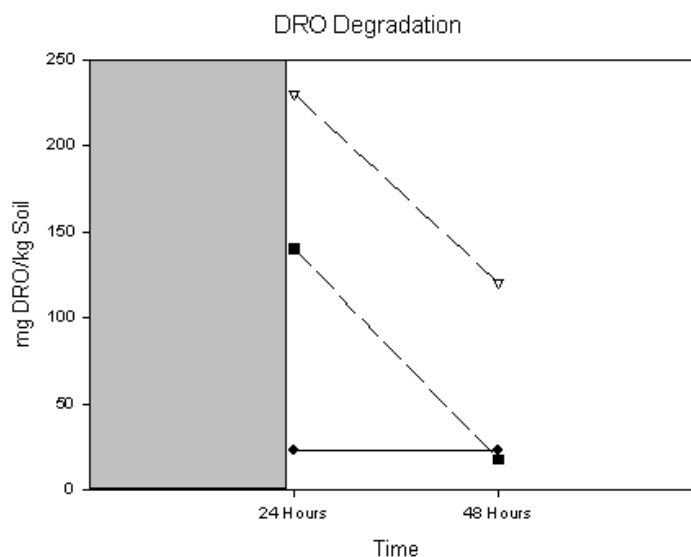
Figure 12.DRO Degradation Following Two Applications of RegenOx Across a 48-h Period. (The control with activator (▼) showed moderate degradation while the treated sample (■) showed the greatest degradation. The control with no activator (●) remained stable across 48 h. The grey area denotes initial reaction time.)

Table 5.Total Extractable Hydrocarbon Concentration (as mg DRO/kg soil) Results from the pH Adjusted Bench Test.

Total Extractable Hydrocarbons	
Sample ID	**Total Extractable Hydrocarbons* (mg/kg)**
Soil #1	2970
Soil #2	3100
Soil #3	2800
RegenOx Treated #1	18.0
RegenOx Treated #2	14.4
RegenOx Treated #3	42.0

All Total Extractable Hydrocarbons were found to be in the Diesel Range

As shown in Table 6, the final concentrations of the treated samples were similar to those found in the previous test. The pH had little effect on the resulting concentrations. By performing baseline analysis, it was determined that diesel could be degraded by 99.2% using the optimal dosage of RegenOx.

The test on the effect of RegenOx on PAHs from coal tars revealed some of the limitations of the technology (Table 6). It was shown from this test that RegenOx effectively releases, and increases the availability of PAHs to oxidation, but fails to effectively oxidize the constituents to a desired level.

Table 6. Resulting PAH Concentrations from the Coal Tar Bench Test.
(The control contained neither oxidant nor activator.)

Compound	Control (ppb)	Treated (1:3 Oxidant: Activator) (ppb)
Acenaphthene	51	122
Acenaphthylene	ND	ND
Antracene	13	38
Benzo(a)antracene	1.8	6.2
Benzo(a)pyrene	ND	1.4
Benzo(b)fluoranthene	ND	2.4
Benzo(g,h,i)perylene	ND	ND
Benzo(k)fluoranthene	ND	1.6
Chrysene	1.7	5.3
Dibenzo(a,h)antracene	ND	ND
Fluoranthene	28	82

Because it was known that the sample contained high concentrations of phenols, a separate test was used to determine if this was affecting the breakdown of the PAHs. The following sets were established for this test:

Set 1: Control (nothing added),

Set 2: pH adjusted control,

Set 3: Control Part B only #1 (Part B concentration of 15,000 ppm),

Set 4: Control Part B only #2 (Part B concentration of 5,000 ppm),

Set 5: Control Part A only #1 (Part A concentration of 5,000 ppm),

Set 6: Control Part A only #2 (Part A concentration of 15,000 ppm),

Set 7: Part A and Part B 1:3 (Part A at 5,000 ppm and Part B at 15,000 ppm), and

Set 8: Part A and Part B 3:1 (Part A at 15,000 ppm and Part B at 5,000 ppm).

The results from this test are shown in Table 7. It was found that, like the PAHs, phenols were being extracted though not oxidized. Further research will be necessary to determine the best technology to effectively decrease the constituents of concern. This could include, but not be limited to, the addition of another oxidant or the introduction of other technologies effective at degrading heavy ended hydrocarbons.

**Table 7. Phenol Results From the Coal Tar Bench Test**

Set	Phenols (mg/L) - Averaged
Control (nothing added)	< 0.008
pH Adjusted Control	< 0.008
Control Part B Only (15,000 ppm)	< 0.008
Control Part B Only (5,000 ppm)	< 0.008
Control Part A Only (5,000 ppm)	0.017
Control Part A Only (15,000 ppm)	0.113
Part A and Part B 1:3	0.037
Part A and Part B 3:1	0.096

In the presence of any oxidant, chromium can become Cr(VI). Since Cr(VI) could potentially pose a health risk, it was important to see what extent a given oxidant in a proposed area would produce Cr(VI). A bench-scale test was undertaken to estimate the initial changes in concentrations of total chromium and Cr(VI) upon application of two oxidizers – RegenOx and H_2O_2. The results from this test are inconclusive, since the sample provided by Regenesis failed to have any Cr present down to the ppb level.

Results from these tests have been useful in showing that RegenOx can effectively degrade diesel when correctly applied. It was also determined that pH has little effect on its degradation. Other tests performed this quarter have shown that PAHs from coal tars are readily extractable, though not oxidized using the reviewed technology. Further tests are necessary to determine the best technique or combination of techniques to obtain the desired concentrations.

Effect of Activator on Other Oxidants

A test was conducted on persulfate for oxidizing contaminants in water systems. Specifically, activation of persulfate was investigated with tetrachloroethene (PCE) as a model compound. Results indicate that RegenOx Part B (an iron containing complex) appears to have a higher efficiency in activating persulfate in PCE oxidation (Figure 13). This finding would be beneficial to modify field applications of persulfate oxidation, which usually uses alkali activators.
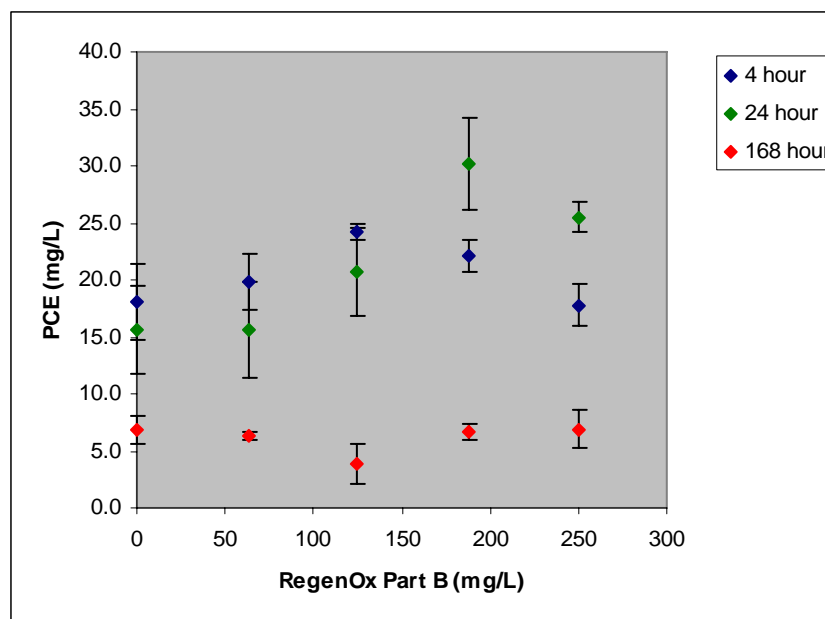
(a)
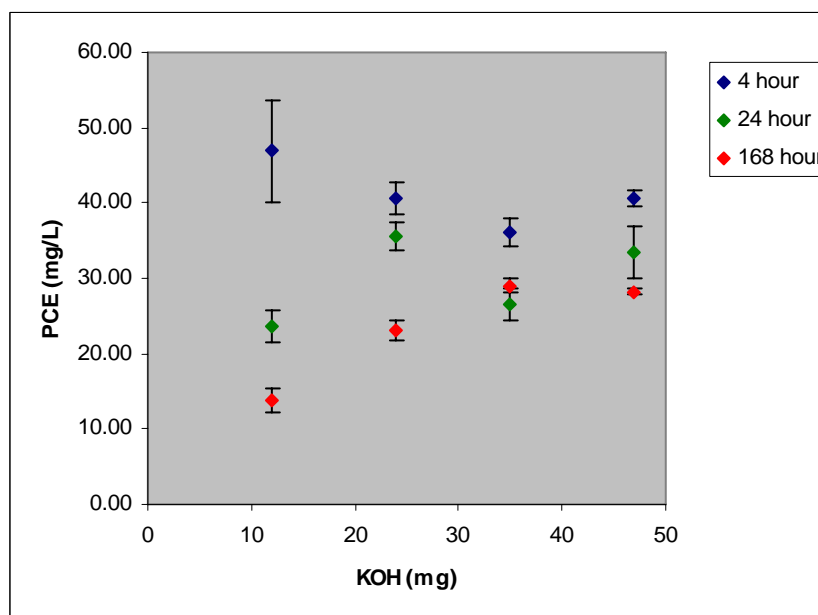
(b)

Figure 13. Activation of Persulfate with RegenOx Part B (a) and KOH (b). PCE concentrations were monitored at 4, 24, and 168 hr. RegenOx Part B achieved higher degradation of PCE during the process.

Treatments for the oxidation of MTBE test are listed in Table 8 where persulfate was added at a concentration of 25,000 mg/l. After 24 hours, MTBE concentrations decreased in all treatments containing persulfate (Figure 14); however, persulfate without activator resulted in lower MTBE concentrations than treatments with activator. All MTBE in oxidant-amended

treatments were removed after 168 hours. These results indicate that persulfate can sufficiently oxidize MTBE without activation from RegenOx Part B.

Treatments for the oxidation of benzene and n-heptane tests are listed in Table 9 where persulfate was added at a concentration of 2500 mg/l. Results indicate that benzene oxidation occurs at higher rate with activation by RegenOx Part B than with KOH activation (Figure 15). However, there was no substantial difference between activation by RegenOx Part B and KOH during oxidation of n-heptane (Figure 16). These results indicate different persulfate and activator performance for each type of contaminant, which indicate that properties and concentration of the contaminant is important consideration when implementing a treatment strategy involving chemical oxidation. Continuing work with oxidation of other types of contaminants at different oxidant concentrations and different oxidants is presently being conducted.

**Table 8. Treatments Description for Tests Involving Oxidation of MTBE
by Persulfate with Different Activator Oxidant Ratios**

Treatment ID	Oxidant	Activator	Activator/Oxidant Ratio
C	None	None	NA
1	Persulfate	None	0.00
2	Persulfate	RegenOx Part B	0.25
3	Persulfate	RegenOx Part B	0.50
4	Persulfate	RegenOx Part B	0.75
5	Persulfate	RegenOx Part B	1.00
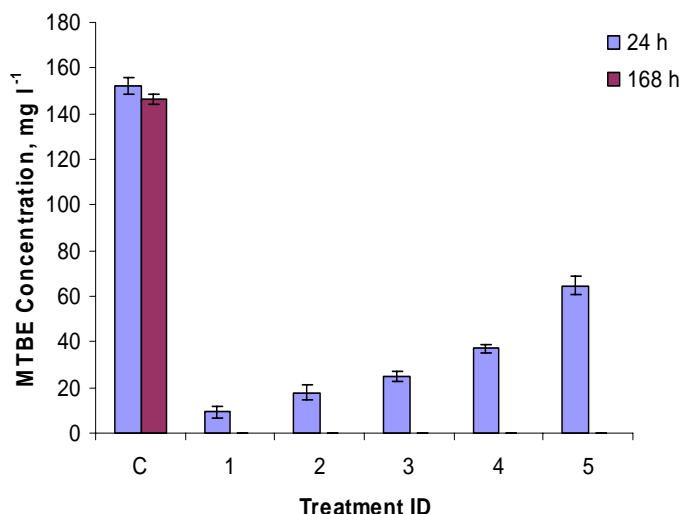
Figure 14. **MTBE Oxidation by Persulfate at Intervals of 24 and 168 h.**

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Table 9.Treatment Descriptions for Tests Involving Oxidation of Benzene and n-heptane (separately) by Persulfate with Different Activator oxidant ratios

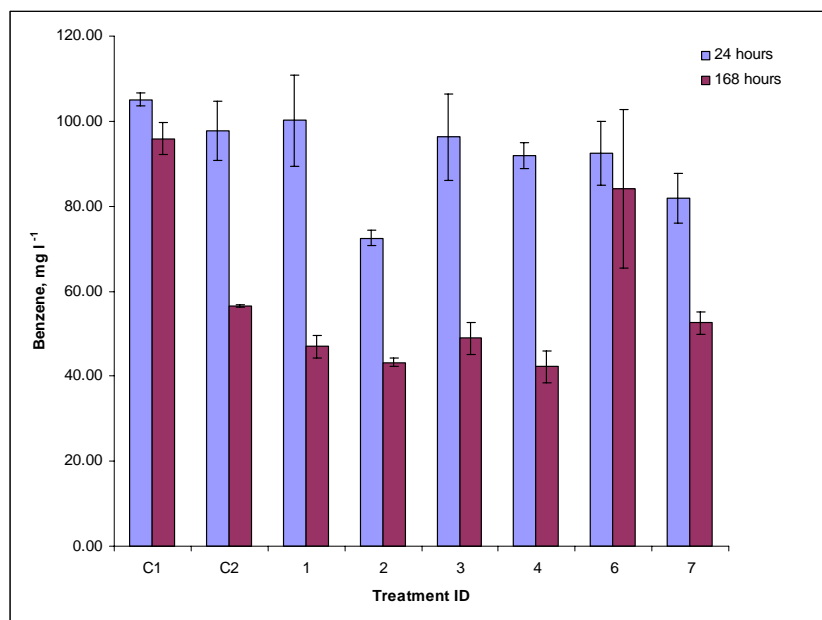| Treatment ID	Oxidant	Activator	Activator/Oxidant wt Ratio
C1	None	None	NA
C2	Persulfate	None	0.00
1	Persulfate	RegenOx Part B	0.25
2	Persulfate	RegenOx Part B	0.50
3	Persulfate	RegenOx Part B	0.75
4	Persulfate	RegenOx Part B	1.00
6	Persulfate	KOH	0.5*
7	Persulfate	KOH	2*

Figure 15. Benzene Oxidation by Persulfate at Intervals of 24 and 168 h
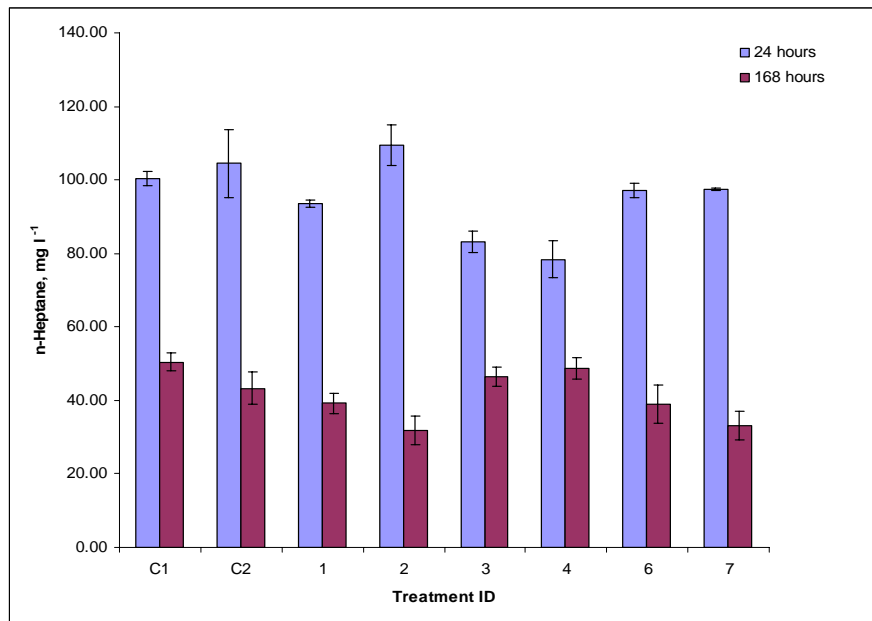
Figure 16. n-Heptane Oxidation by Persulfate at Intervals of 24 and 168 h

SUMMARY

Western Research Institute, in conjunction with Regenesis and the U.S. Department of Energy, conducted a study that investigated the performance of a "safe" oxidant, SPC, to cleanup groundwater and soils contaminated with petroleum hydrocarbons and associated contaminants (e.g., MTBE). Results from a field pilot test in Frenchglen, OR, showed VOC concentrations in groundwater decreased substantially within 2 weeks after injecting activated SPC (RegenOx). However, concentrations rebounded due to the consumption of the oxidant and the plume movement. A protocol was established for determining RegenOx TOD in soils and groundwater. Total oxidant demand tests were necessary to determine the correct dosage of RegenOx to apply in the field and sufficiently degrade the contaminants of concern. Tests were performed to validate the TOD method where soils contaminated with diesel fuel and PAHs were used. Results of these tests also indicated little to no mobilization of metals occurring with an overdose of RegenOx. Bench studies with RegenOx showed this technology was effective in degrading diesel fuel and 1,4-dioxane. However, the results for individual PAHs are inconclusive. The Fe-silica activator (RegenOx Part B) was tested with another oxidant, sodium persulfate. Bench tests results showed the combination of sodium persulfate and RegenOx Part B was effective in reducing PCE, MTBE, benzene, and n-heptane concentrations in water. Overall, the results of this project indicated that most petroleum contaminants in soil and groundwater can be sufficiently degraded using the RegenOx technology. Also, an important TOD protocol was established to maximize the performance of RegenOx in field applications.

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APPENDIX A.

Standard Protocol for Determination of Total Oxidant Demand (TOD)

Materials Required:

- 10 g Site Soil
- 100 mL Site Groundwater or RO Water
- 150-mL clear or brown-glass jar w/lid
- RegenOx - Part A and Part B
- 10-ml, luer-lock syringe
- Glass Wool
- 0.45 μm syringe filter

1. Weigh 10 g of site soil into a 150-ml clear or brown-glass jar and add 80 mL of site groundwater or RO water. Seal jar tightly and mix well. Allow mixture to react for at least one hour before step 2.
2. Weigh 0.1 g of RegenOx Part B into a weighing cup. Add 10 mL of site groundwater or RO water to the weighing cup and mix well. Add solution to the jar and mix well.
3. Weigh 0.1 g of RegenOx Part A into a weighing cup. Add the remaining 10 mL of site groundwater or RO water into the weighing cup and mix well. Immediately add the solution to the jar and mix well.
4. Immediately take a two-stage filtered sample (first stage: glass wool; second stage: 0.45 μm) to be analyzed as a time zero sample, using the UV Spectroscopy Method (see below).
5. At 4 hours take an additional two-stage filtered sample (as described above) to analyzed using the UV Spectroscopy Method (see below).
6. Determine TOD by subtracting concentration of 4 hour sample from concentration of time zero sample.
7. Repeat steps 1-5, substituting 1.0 g of RegenOx Part A & Part B.

UV Spectroscopy Method (for determination of RegenOx (sodium percarbonate))

Materials Required:

- Reagents:
  - 0.46% Titanium (IV) oxysulfate ($TiOSO_4$)
  - 9 M sulfuric acid
  - 100, 250, and 500 ppm RegenOx and RegenOx & Activator solutions
- 25-mL volumetric flasks

NOTE: Original method was developed using 10-mL volumetric flasks

<u>Developing the Calibration Curves</u>

<u>**NOTE**</u>: Repeat the following procedure to develop a calibration curve for RegenOx & Activator by substituting RegenOx solutions with RegenOx & Activator (i.e. 100 ppm, 250 ppm and 500 ppm).

1. Add 2.5 mL of 0.46 $TiOSO_4$ and 6.25 mL of 9 M H_2SO_4 to four 25-mL volumetric flasks.
2. Add 2.5 mL of the 100 ppm RegenOx solution to one flask. Add 2.5 mL of 250 ppm solution to another flask. Add 2.5 ml of 500 ppm solution to another flask. The remaining flask will be used as a blank.
3. Bring all four flasks to volume with DI water, and heat at 60°C for 10 min. Let cool to room temperature.
4. Zero spectrophotometer with the blank at 407 nm.
5. Measure absorbance of the other three at 407 nm. Use table A-1 as a template.

Table A-1Template to develop calibration curve for determination of RegenOx and RegenOx & Activator.

	Concentration (mg)	Absorbance at 407 nm
	0.000	
RegenOx	0.250	
	0.625	
	1.250	
RegenOx &Activator	0.250	
	0.625	
	1.250	

6. Plot RegenOx and RegenOx & Activator concentrations versus absorbance at 407 nm. Figure A-1 contains sample calibration curves produced by WRI.
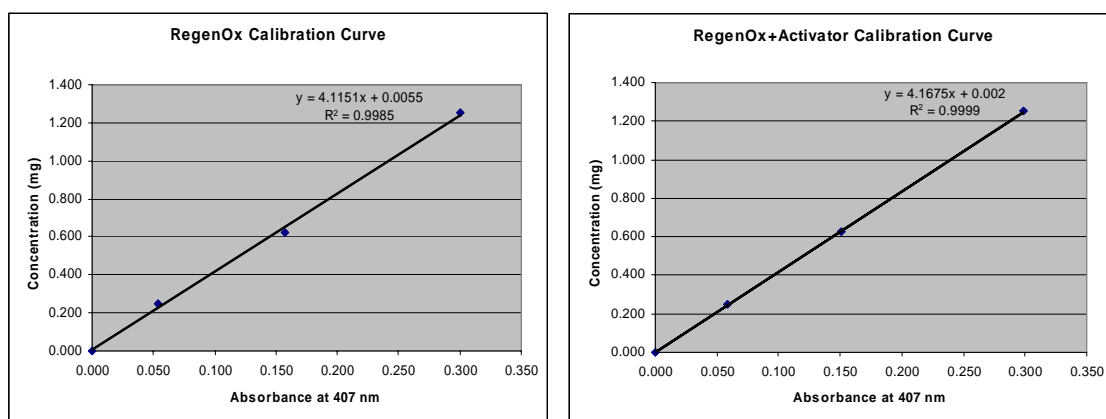

Figure A-1. Sample calibration curves developed using the UV spectroscopy method by WRI on 7/2/2005

Testing Samples

1. Add 2.5 ml of 0.46 TiOSO$_4$ and 6.25 ml of 9 M H$_2$SO$_4$ to a 25-mL volumetric flask.
2. Add 2.5 ml (less or more, depending on sample concentration) of sample to the flask. Bring to volume with DI water.
3. Heat at 60°C in a water bath for 10 minutes. Let cool to room temperature.
4. Measure absorbance at 407 nm.
5. Calculate concentration from calibration curve.