

Performance of Enhanced Aerobic Bioremediation on Remediating Upstream Oilfield Wastes

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Abstract

Accelerating degradation rates and reducing treatment times can improve the utility of bioremediation. This paper discusses an enhanced aerobic bioremediation process that accomplishes these goals using a chemical agent blended with nutrients. By increasing contaminant solubility and bioavailability, the chemical agent augments the capacity for contaminants to be metabolized.

Case studies are presented that demonstrate, with proper treatment and maintenance procedures, the enhanced aerobic bioremediation process is effective in treating invert diesel mud and drill cuttings. Field trials have achieved contaminant mass reductions ranging from 67-95% within 3-5 days.

Introduction

Bioremediation occurs in nature at slower than desirable rates for most remedial corrective action and the most widely accepted bioremediation methods, land treatment and composting, are considered by industry to be medium-to-long term approaches. A recognized limitation of these technologies is the potential for contaminant degradation to stall out at asymptotic limits above cleanup guidelines. This issue has come under scrutiny with focus on more stringent regulatory limits on upstream oilfield wastes.

The enhanced bioremediation technology offers an alternative to conventional methods. Like land treatment, a key element in the process is its reliance on the native soil bacteria. A percentage of the indigenous microbes are usually well suited to affecting hydrocarbon transformation. They are already acclimated to the environment and, where soils have been impacted, to the contaminant. In studies where non-indigenous microbes have been introduced, cultures have not competed well with native populations. Other research found no evidence supporting the use of non-native microorganisms as being significantly beneficial (USEPA, 1995).

The effectiveness of bioremediation depends on environmental factors such as available oxygen, moisture content, nutrient supply, pH and temperature. Aerobic bioremediation generally proceeds rapidly and results in a more complete degradation of organic constituents. In the presence of sufficient oxygen and nutrients, microorganisms will ultimately mineralize organic contaminants to carbon dioxide, water and microbial cell mass.

An improper balance of these critical environmental factors can slow down or stop the bioremediation process. Other factors such as high contaminant concentrations or acidic and alkaline environments can create toxic conditions inhibiting bioremediation.

Overview of Enhanced Bioremediation Process

Process Chemical Agent.

The chemical's base formulation contains a hydrophilic non-ionic surfactant that is 100% biodegraded after sixteen (16) days in aqueous solution (**Figure 1**). The chemical agent remains potent for up to fourteen (14) days and partitions petroleum hydrocarbons by forming microscopic micelle that result in increased contaminant solubility and bio-availability. Surfactant solubilization significantly increases the aqueous concentration of the contaminant by micellar partitioning. Bioavailability is achieved by mobilization which effects interfacial tensions to significantly reduce the capillary forces trapping the hydrocarbon, thereby allowing hydrocarbons to be readily extracted (USEPA, 1996).

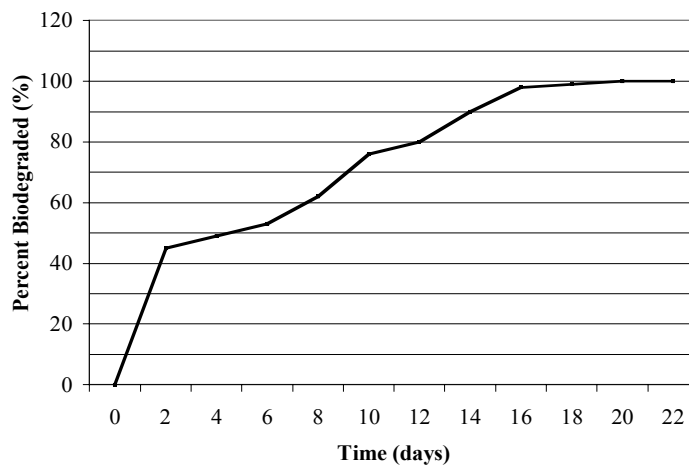


Figure 1. Chemical Agent Biodegradability

Table 1. Trout 96h Static Acute Test-Trout (*Oncorhynchus mykiss*)

Time (days)	pH	EC(uS/cm)	DO(mg/l)	Temp ($^{\circ}$ C)	No. Alive
0	8.1	352	8.7	15	6
1	8.3	355	9.0	16	6
2	8.3	359	8.7	16	6
3	8.2	366	8.6	16	6
4	8.2	367	8.4	16	6

Research projects evaluating the use of surfactants have resulted in mixed reviews depending on the contaminant substrate present, the type of surfactant used, speculated causes of biodegradation inhibitors and the desired results. A concern when considering the applicability of a particular surfactant is its potential environmental impact.

Land usability and protection of groundwater aquifers are paramount concerns when applying chemical products. Laboratory toxicity testing on *Mysidopsis Bahía* shrimp and trout bioassays (**Table 1**) has demonstrated the chemical agent is non-toxic at recommended treatment concentrations.

The results of post-treatment leaching studies conducted in the soil profile beneath treatment zones suggest the degraded chemical agent does not release contaminants to adversely effect groundwater aquifers.

The chemical is also listed on the U.S. Environmental Protection Agency's NCP Product Schedule as a "Surface Washing Agent". This listing does not constitute an USEPA endorsement of product use. It only indicates that data has been submitted to the USEPA as required by subpart J of the National Contingency Plan section 300.915.

Process Treatment.

Contaminated material is typically treated in biocells spread to a uniform thickness of 15-20 centimeters (6-8 inches). A native soil amendment is incorporated into the waste to introduce indigenous microorganisms needed for bioremediation. The mix is then treated topically with a 5-7% solution of chemical agent. Tilling is conducted until a homogeneous slurry is attained. The mix's consistency assures adequate contact between the microorganisms, the chemical agent and the waste and optimizes moisture content and dissolved oxygen levels. Critical environmental factors are monitored during treatment and adjusted by additional water application and tillage to keep treatment moisture content within a range of 30-40% by volume, pH near neutral and dissolved oxygen at levels greater than 2.0 mg/l.

The addition of native soils causes some skepticism with the process because of an apparent remediation due to dilution. Typical waste-to-soil mixing ratios result in a 12-20% dilution or less if the soil amendment also contains residual contaminants. Final concentrations reached in field trials treating wastes exhibiting 3-20% hydrocarbon mass by weight can not be accounted for by dilution alone. Ultimately, the waste/soil mix will depend on the initial waste concentration (toxicity) and the number of microorganisms determined from heterotrophic plate count data.

Compared to soil dilution, dilution by water results in minor changes in hydrocarbon concentration. Most upstream oil field waste is comprised of longer-chained hydrocarbons. Research by the Total Petroleum Hydrocarbon Criteria Working Group showed that, in higher carbon-number (>10) hydrocarbons most of the mass for either aliphatic or aromatic hydrocarbons is sorbed to the soil (TPHCWG, 1997).

Process Performance.

The cleanup of upstream oilfield wastes focuses on the degradation of free-phase and adsorbed-phase contaminants. Generally, low molecular weight compounds partition to the aqueous and gaseous phases while high molecular weight compounds have a propensity to be less soluble and be more adsorbed (recalcitrant) with increasing carbon number. Chemical structure also controls the ease at which hydrocarbon compounds can

be biodegraded. Residual petroleum hydrocarbons at initially low concentrations may not be capable of supporting significant microbial activity even after stimulation. Therefore, projects with relatively high petroleum hydrocarbon impact may be better candidates for bioremediation.

The benefits of using the chemical agent include an increased growth in microorganisms without the need for additional nutrient amendments and accelerated hydrocarbon degradation rates. The responses to the chemical by these factors are presented in **Figure 2** and **Figure 3**.

Figure 2 represents postings of baseline standard plate counts in the native soil and accelerated populations after initial treatment. The values need to be multiplied by 10^6 to obtain the actual standard plate count in units of CFU/gm soil. As shown on the figure, microbial population increases of 2-3 orders of magnitude have been observed. This increase usually occurs within the first few days of treatment. While commercially available nutrient amendments can achieve similar results, **Figure 2** shows the chemical agent's capability in providing this key process ingredient of a sufficient viable biomass so bioremediation can proceed.

Remedial results that can be expected during treatment are shown in **Figure 3**. The first bar in each grouping is the hydrocarbon reduction measured after 3-5 days of treatment and the second bar is the total reduction achieved at the time the test was terminated. There are no final reductions posted for treatments 2 and 6 because the cleanup goal was reached within five days of application. The initial reductions range from 67-95% and average 82 percent. Stated differently, if cleanup standards for a project are approximately 20% of the residual petroleum hydrocarbon concentrations, the enhanced

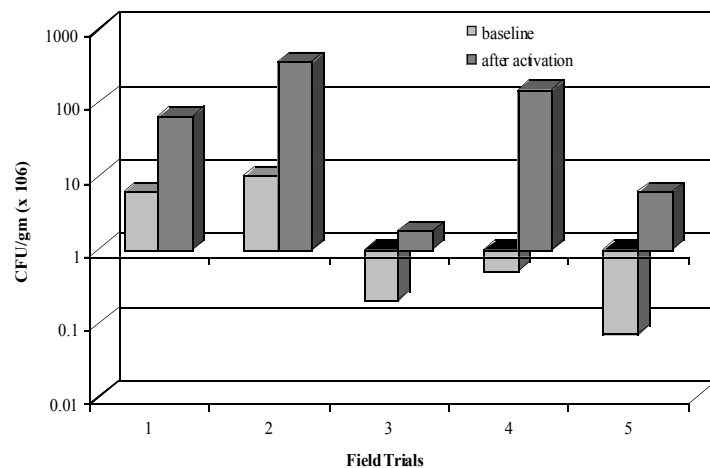


Figure 2. Chemical Effect on Microbial Populations

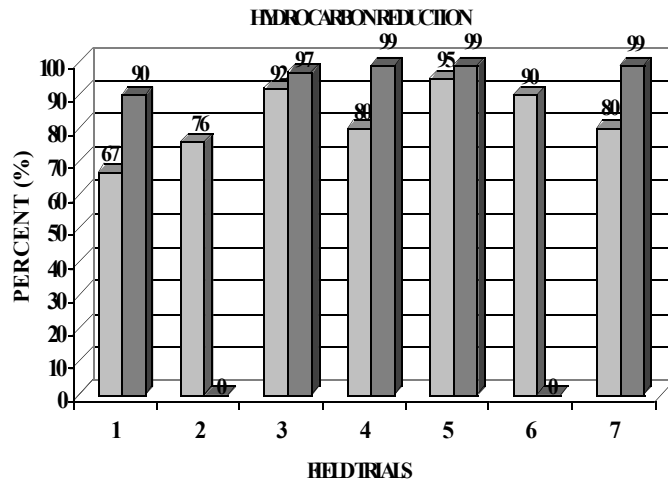


Figure 3. Chemical Effect on Hydrocarbon Concentration

bioremediation process can usually achieve cleanup within 3-5 days. Cases Study 1 will demonstrate the decrease in concentrations reflect real contaminant mass reduction.

A typically observed degradation of a diesel mixture is presented in **Figure 4**. Correlation analysis of the concentration curves show that the percentage of contaminant reduction is similar across all carbon fractions with the exception of the C10-C12 fraction that was

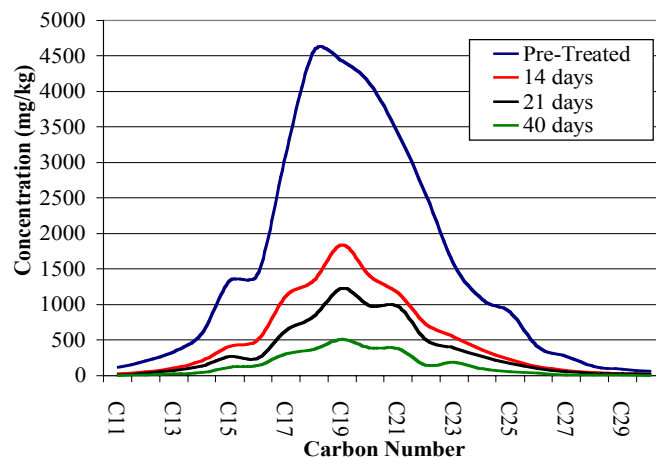


Figure 4. Hydrocarbon Degradation

reduced by 83% in the first seven days of treatment. The narrowing of the gap between concentration curves with time is reflecting the degradation rate change depicted in **Figure 5**. Field trials consistently show initial rapid reductions changing to an apparent constant rate within one to two weeks after application.

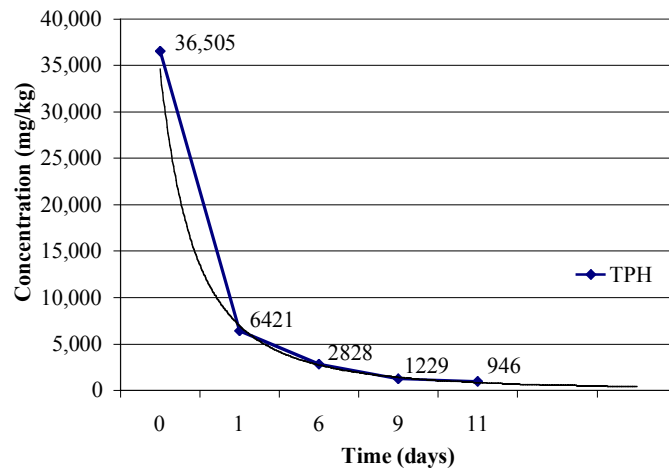


Figure 5. PHC Degradation Curve

Case Studies

Case Study 1-Controlled Field Trial

Background.

A controlled field trial was conducted to evaluate the efficacy of the chemical as a bioremediation agent. Since the chemical's base formulation contains a surfactant, the test was designed for the collection and analysis of leachate to account for all potential loss mechanisms. The test was divided into control and treatment plots. The test was conducted for a period of one week and samples were collected at time $t = 0$, 1.5 hours, days 1-3 and at the end of the test.

During the field trials daytime ambient temperatures were measured, on the average, at 32°C (90°F). Overnight temperatures dropped to 24°C (75°F). Weather conditions were generally sunny with scattered clouds.

Field Trial.

A biocell treatment unit was constructed and divided into a control and a treatment cell. Both cells were constructed with a 40-ml geomembrane and a leachate collection system. Prior to loading, the raw waste, an oil-based drilling mud, was blended with sandy loam soil which attained a 3.5% and 3.2% petroleum hydrocarbon (PHC) mix in the control

and treatment cells, respectively. After spreading, the contaminant in the treatment cell was treated topically with the chemical agent at the application rate shown in **Table 2**. Water was the only additional amendment applied to the control cell. Similar tilling and watering practices were conducted in both cells during the field trial. Initial cell activation resulted in the test plots having a 20% percent moisture content by weight.

Table 2. Case Study 1-Application Rates

Test Plot	Amendments	Application Rate (L/m ³)	Application Ratio
Control	Soil, Water	NA	NA
Treated	Soil, Water, Chemical	7.6 (2 gals)	1:20

Composite soil samples were analyzed on-site using a retort and at an independent laboratory by gas chromatography. When present, leachate samples were collected and analyzed for PHC. During the test hydrocarbon concentrations, microbial activity, soil volume, amendments, pH, chlorides and moisture content were monitored.

Performance.

The initial drop in PHC levels shown in **Figure 6** and **Table 3** for the control cell was caused by the incorporation of soil during initial tilling practices. The slight PHC concentration increase at day 2 was in response to decreasing moisture content. The first decrease in PHC concentration corresponding to contaminant mass reduction occurred at day 3. The overall reduction in contaminant mass in the control cell during the test was

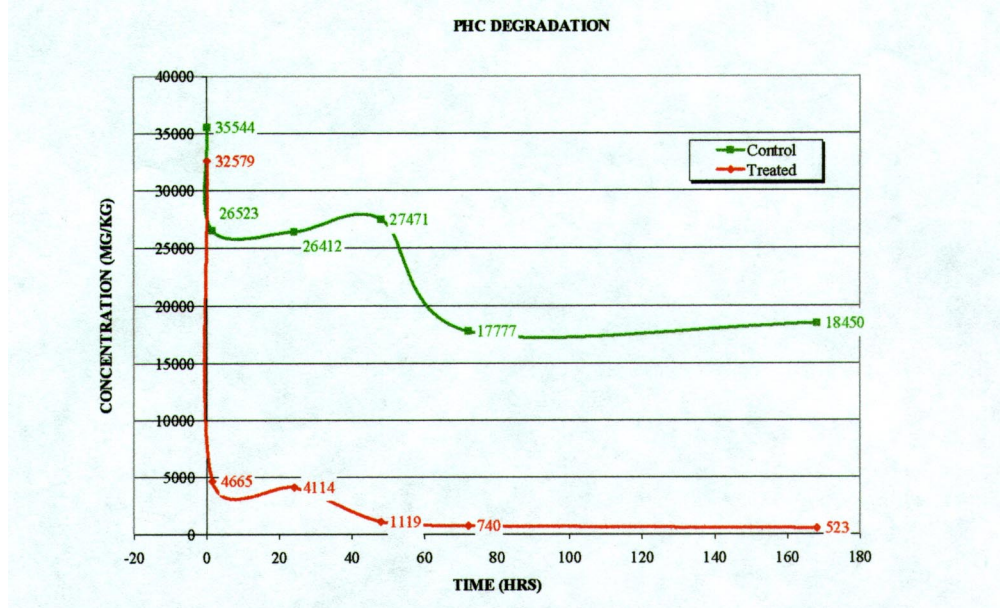


Figure 6. Petroleum Hydrocarbon Concentration Reduction

Table 3. Case Study 1-Control Cell PHC Reduction

Time		S.A.	MC	Contaminant	Mass
	FID	Volume		Mass	Reduction
Hrs	mg/kg	x initial	%	kg	%
0	35544	1	14.9	41.0	0.00
1.5	26523	1.3	20.7	41.0	0.00
24	26412	1.3	16.8	41.0	0.00
48	27471	1.3	15.4	41.0	0.00
72	17777	1.3	15.4	26.6	35.1
168	18450	1.3	11.4	26.6	35.1

Table 4. Case Study 1-Treated Cell Reduction

Time	GC	S.A.	MC	Contaminant	Mass
	FID	Volume		Mass	Reduction
Hrs	mg/kg	x initial	%	kg	%
0	32579	1	13.3	37.6	0.00
1.5	4665	1.25	21.0	6.7	82.2
24	4114	1.32	18.1	6.3	83.2
48	1119	1.32	19.5	1.7	95.4
72	740	2	18.2	1.7	95.4
168	523	2	16.1	1.2	96.8

35%. Corresponding treatment results are shown in **Figure 6** and **Table 4**. Twenty-three percent (23%) of the initial drop in PHC concentration is due to mixing; the remainder is loss of contaminant mass. The hydrocarbon concentration decrease between day 2 and day 3 is completely accounted for by dilution factors. Comparing the 96% reduction in the treated cell with results attained in the control cell, the data shows the chemical achieved 61% more hydrocarbon degradation than the control conditions.

Case Study 2-Alberta, Canada.

Background.

A treatment cell was constructed in July 1998 to address the waste management of invert diesel drill cuttings. The cell was built to accommodate three windrows. The drill cuttings were mixed with bulking agents and nutrient amendments to decompose the waste by composting. After two years of treatment, data collected during the last eight months suggested that the residual PHC concentrations may be representative of an asymptotic concentration limit.

Petroleum hydrocarbon concentrations (PHC) in the windrow were measured at 30,600 mg/kg. Of this composition, the C10-C12 fraction (316 mg/kg) represented one percent

of the mix, the C12-C16 fraction (2,273 mg/kg) represented seven percent, the C17-C21 fraction (21,000 mg/kg) represented sixty-nine percent and the C22-C30 fraction (7,011 mg/kg) represented twenty-three percent. The volatile C3-C10 fraction was not detected by laboratory analysis. This was not unexpected given the mix had already been composted for two years.

Field Trial.

A new treatment unit was constructed to accommodate 120 m³ (157 cubic yards) of contaminated drill cuttings. Prior to construction, the receiving subsoil was sampled on a 10 m³ grid pattern along with the windrow cuttings to establish baseline conditions. After spreading, the drill cuttings were treated topically with a chemical/water ratio of 1:15. During treatment, the top 5 cm (2 inches) of subsoil was incorporated into the pile. With a treatment unit area of 842 m², this practice resulted in a 3:1 (120 m³: 40 m³) mix. Based on these volumes, the initial 30,600 mg/kg concentration was lowered to 21,600 mg/kg (**Table 5**) without any reduction in contaminant mass.

Tilling continued until the microorganisms in the soil were adequately mixed with the waste. The treatment unit was sprayed with a total of 330 gallons of chemical agent and 12,900 gallons of water over two days.

Composite sampling of the waste was conducted weekly to monitor petroleum hydrocarbon degradation rates and microbial populations. Tilling was performed weekly to promote aeration and to maintain a homogeneous slurry. The ranges exhibited in operating parameters during the test are listed in **Table 6**.

Table 5. Case Study 2- Initial Hydrocarbon Reduction

Media	Volume m ³	Density Kg.m ³	Concentration mg/kg	Cont. Mass Kg
Compost	120	1200	30,600	4,406.4
S. A.	40	1500	0	0.0
Pre-Treat Mix	160	1200	21,600	4,406.4
3.5 hr Sample	160	1200	17,000	3,264.0

Table 6. Case Study 2-Operating Parameters

Parameter	Value
Mixing Frequency	Weekly
Moisture Content (treatment zone)	18 - 31 %
pH (treatment zone)	7.1-7.6
Residence Time	28 days
Temperature	Ambient

Performance.

Standard plate counts posted in **Table 7** document the immediate stimulation of the indigenous microorganisms. A second order of magnitude increase in the number of microorganism colonies occurred after the initial application. Colony counts remained at elevated levels for seven to ten days before decreasing in populations. The decrease cor-

Table 7. Case Study 2-Performance Data

Sample ID	Hydrocarbon (mg/kg)	Plate Count	pH	EC	SAR	Moisture Content
Waste-Initial	30,600	10 x10 ⁶	7.1	3.7	3.4	31%
3.5 hrs	17,000	365 x10 ⁶	---	---	---	---
7days	9,930	112 x10 ⁶	7.1	2.0	1.9	---
14 days	10,300	---	7.6	1.3	1.2	24%
21 days	6,970	33 x10 ⁶	---	---	---	---
28 days	3,720	3 x 10 ⁶	7.6	1.4	1.2	18%

related with a lowering of contaminant levels suggesting the microbial populations were returning to background levels as the hydrocarbon food source was being depleted.

Table 7 further shows the enhanced ex-situ bioremediation application reduced the hydrocarbon concentration by 88% in twenty-eight days and resulted in a hydrocarbon content of 0.37% by dry weight. The flat lining of the concentration curve observed in **Figure 6** between day 7 and day 14 was suspected to be related to oxygen depletion and a drop in moisture content associated with an observed encrusting of the treatment pile surface.

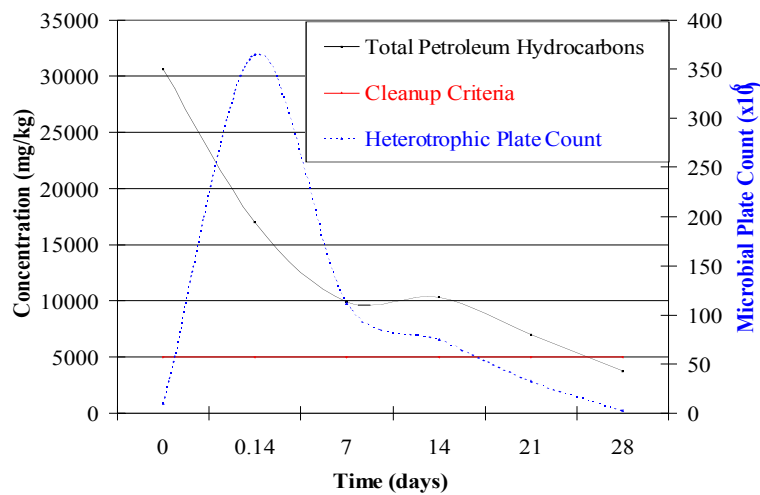


Figure 6. Oil-Based Drill Cutting Remediation vs Time

Unlike Case Study 1, a control cell was not constructed for this project. However, a tractor and rotospic was used during process maintenance which allowed the operator to control the tilling depth within tolerance. Collected data (**Table 5**) documents an initial 26% contaminant mass reduction within the first three hours after application. Using a tillage tolerance of 5 cm (2-inches), it is reasonable to assume the post trial hydrocarbon concentration would represent a 62-84% reduction in contaminant mass.

Conclusion

Bioremediation is a technology whose use has been proven effective in the cleanup of contaminants for several years. One should be cognizant that this enhanced process is not a panacea for the cleanup of all contaminants but performs well at remediating petroleum hydrocarbons.

This paper demonstrates through field-based case studies that when a favorable environment for bioremediation is maintained, enhanced aerobic bioremediation can successfully treat petroleum hydrocarbons and is an improvement on well-established bioremediation practices.

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