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Environmental Remediation Using Advanced Microbial Techniques

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Abstract

Objectives/Scope: An ongoing issue for many operators is the need to be able to safely and quickly remediate environmental issues. Of particular interest are the cleanup of petroleum products, and the cleanup of produced water, which often has extremely high levels of Chlorides (Cl-), and may include hydrocarbon components. This paper will discuss a methodology that has been applied in over 1400 locations

Methods, Procedures, Process: Methods used in the past have been difficult and expensive, often causing issues with the disposal of contaminated soil.

Attempts have been made for many years to perform in-situ remediation. In the 1950's, processes were developed that enhance the growth of naturally occurring microbes by applying a culture of microbes and enzymes to the affected area.

The process studied has been used in over 1400 individual locations, providing a rich data set for analysis. Differences in how the processes were executed have resulted in variances in the results and the scope of the treatment required to meet environmental standards. This paper will document the work, and identify features and techniques that enhanced or diminished success rates. Processes will then be optimized to maximize the consistency of results at minimum cost.

Results, Observations, Conclusions: Six treatments are described in this abstract as representative examples of the effectiveness of the process. The first treatment reviewed involved remediation of a wellsite in West Texas near Garden City, TX. The treatment resulted in reductions of Cl- contamination by 83% to 99%. The second treatment reviewed was completed on another site near Garden City, TX where a produced water spill had contaminated cotton fields. Reduction of contaminants at this site was over 99%. The third treatment reviewed was a site in Fisher County,

TX, where a spill contaminated a pond on the site. Reductions of Cl- up to 84% were observed, and hydrocarbon contaminants were reduced over 99%. The fourth description involves a site in Gaines County, Texas that experienced a produced water spill in April 2016. As a result of the spill, the initial contamination of the soil was tested to be 30,000 PPM. The area was treated using the process and the biological agent. Within twenty-one days, the salt level in the soil had been reduced to 900 PPM. Local plant life was observed to be growing in the formerly contaminated soil within twenty-eight days. The fifth description involved a site in Fisher County, Texas, where a pipeline leak contaminated soil. Samples were taken at several locations at the surface, and at depths of 48" and 60" to evaluate ground penetration. Post treatment samples indicated reductions of 57% to 99.99%. The sixth description involved a site in Jal, New Mexico where crude oil was spilled into a storm sewer, and the oil flowed into a sewage treatment plant. The site and the sewage plant were treated, and reductions of hydrocarbons were observed to be 98%-99% of the original sample values.

The processes described in this paper offer a significant benefit not only to the oil and gas producing community, but also to the general public in that the ability to restore previously damaged soil enhances the environment we live and work in.

Historical Background

In the early days of the petroleum industry, little was known about the environmental impact of petroleum products on the environment. Open pits were used at times to store produced fluids and spillage was an acceptable cost of doing business. In those days, the only economic cost was the loss of saleable product. In the years since then, we have become much more aware and sensitive to the environmental impact that petroleum products and produced waters have on the environment, and an understanding of how those issues can have an economic impact on an operator. The increased use of hydraulic fracturing has introduced new variables into the situation.

As a result, stringent regulatory requirements have been put in place to mitigate the impact of incidents involving the release of produced fluids to the environment. The cost of compliance and remediation has become a significant impact to the bottom line of producing operators. An ongoing issue for many operators is the need to be able to safely and quickly remediate environmental issues that have occurred. Of particular interest are the cleanup of petroleum products, both crude and refined, and the cleanup of produced water.

Why is Produced Water Important?

Depending on the reservoir drive mechanism, significant volumes of water may be produced during the life of a well. In addition to some level of hydrocarbon contamination, produced waters often contain extremely

high levels of Chlorides (Cl^-) and metallic elements, which can be toxic to plant and some animal life. As a producing well matures and eventually reaches the end of productive life, the proportion of produced water in the stream (commonly called watercut) can increase to the point that the volumes of produced water that must be handled and treated make it uneconomical to continue operating the well. At this point, the well may be either shut-in, or eventually plugged and abandoned. Shutting in a well is a temporary solution, but may contain the problem until more effective solutions can be employed. Ultimately, an uneconomic well will be plugged and abandoned, which requires additional regulatory permissions and attention to ensure that the abandoned well does not become a problem in the future.

A newer concern is the result of the expansion of the use of hydraulic fracturing to stimulate flow in shale gas reservoirs in recent years. Although "fracing" has been safely used in the petroleum industry for many decades, the scale and scope of usage has increased in recent years. In addition, it has become a cause célèbre for people who don't understand the process or oppose it for political reasons, and a significant amount of incorrect information has been distributed to the public. The water produced after a frac treatment includes formation fluids, but also includes significant volumes of water that were injected during the treatment process, and chemicals that are added to the treatment water to enhance or facilitate the treatment. Most of these substances will be produced by the well during the frac cleanup period, but recovery declines in much the same way production declines in a producing well, so that measurable levels of contaminants may be present for some time.

The Production Operation

To understand the impact of produced water, you need a basic understanding of the production operations process. It is assumed that SPE readers are sufficiently familiar with the various processes associated with production operations that no additional explanations are needed. The primary points of concern for spills of any type include the wellsite, tank batteries, flowlines, and pipelines, and the activities that take place at those points.

These components of Production Operations contain water and other fluids that usually have very high levels of Chlorides, and may also contain trace amounts of hydrocarbons and other pollutants.

Regardless of the source, the handling of produced water involves some level of risk, and results in a not insignificant cost to the operator.

Wellsite Spills

The normal treatment of produced fluids is a relatively straightforward process that is normally performed without releasing fluids to the environment. However, during the normal day to day operations, inevitably some spillage occurs. Well sites are usually built using techniques that provide containment for routine leakage using pit liners or clay shields. Prudent operators make every effort to minimize and remediate routine leakage as a matter of practice, but even the best operators sometimes have spills, either at the well site or on pipelines and flowlines that carry petroleum fluids.

Spillage can occur not only at the wellhead, but also on pipelines and flowlines that transport the products from one location to another. A search of the internet shows that these incidents occur on a regular basis, releasing petroleum products to the environment. The industry generally has a good record of responding to these incidents, but they still happen from time to time. Regulatory agencies such as the Texas Railroad Commission expend significant resources in monitoring and tracking operator performance in the environmental area.

Remediation Steps

The remediation of spills requires that as much of the petroleum product be recovered as possible, and that the contaminated soil and equipment be either cleaned or removed. Depending on the composition of the fluid, some lighter components may evaporate, leaving only the heavier less volatile hydrocarbons. The decision to remove the contaminated soil ultimately requires that you either remove the contaminated soil for treatment elsewhere, or attempt to treat the contamination in place. The cost of treatment can vary widely depending on the areal extent and the depth of penetration into the soil.

The first step in any recovery process is usually the removal of any standing pools of fluids. Vacuum trucks are able to remove any visible liquids as well as any fluids applied during the cleanup process. Depending on the type of soil, liquids may penetrate the soil that makes it necessary to remove the soil to remediate the contamination.

Soil removal can be difficult and expensive, often requiring the removal of large quantities of soil, with the attendant issues in transporting and disposing of the contaminated soil, commonly called "cut and haul". The contaminated soil is scraped up using conventional earth moving equipment, loaded into trucks, and transported to a waste site where it can be either stored or processed for further contaminant removal. Although this solves the immediate problem, it does not eliminate the contamination...it merely moves it to a more convenient location. Transportation risks are always present and the liability of the contaminants remains.

Attempts have been made for many years to attempt "in-situ" remediation of contaminated soil, but the results have been mixed. To address this problem, we have worked with suppliers and engineers to develop a methodology that works, and engineered the process so that it may be made repeatable and used economically. In addition, we have developed equipment that more effectively delivers the remediation processes, and thus promotes in-situ activity. We have investigated and reviewed several biological remediation techniques that indicate that we can reduce the environmental impact of both the contamination and the remediation process.

Virtually all the testing we have done has shown a reduction in the concentrations of testable Chlorides, Total Petroleum Hydrocarbons (TPH), as well as caustics and heavy metals. We have also seen evidence that these pollutants do not return over time, indicating that they are either sequestered or transformed into benign states. We have observed significant plant growth, providing additional confirmation that the effects of Chloride/TPH pollution have been successfully mitigated on a long-lasting basis.

Microbial Bioremediation

In the environment, there are microorganisms, plants or biological enzymes that live or exist naturally in the soil. Typical microorganisms of interest included fungi, yeasts, algae, bacteria, and protozoa. Some species, called anaerobic, are able to live without the presence of oxygen, and in fact there is evidence that the present levels of oxygen in our atmosphere are the result of oxygen produced as a "waste" product by anaerobic bacteria. A second type of species, called aerobic, thrive in the presence of oxygen, and increase in numbers as more and more oxygen is released to the environment. A third group of species are known as facultative anaerobes, and have a unique capability to live with or without oxygen. Many microbes also have the capability to become dormant in situations where their preferred nutrition source is unavailable, and are thus able to survive in areas where the required food supplies may be intermittent. Some microbes also use the process of photosynthesis to process nutrients, so sunlight can play a major role in microbial activity, and needs to be accounted for in the laboratory testing. The objective of the laboratory testing is to understand and mimic microbial behavior in contaminated soils by considering factors such as percent clay mineral, pH, conductivity, temperature, and oxygen availability.

By collecting and combining the three types of microbes in a mixture, the benefits of all three can be realized with the application of one solution. The challenge is in identifying and growing the optimum mixture of microorganisms. Since all of these microorganisms are already present in our environment, we are using what is already in the environment to treat the environment.

Some microorganisms have a unique capability to break down hydrocarbon compounds through normal biological processes. They are unique in that they can consume what would normally be considered pollutants such as petroleum products, and Chlorides (Cl-), converting them to benign components, or "sequestering" them so that they no longer migrate through the soil via groundwater movement. Beneficial processes include oxygen production, nitrogen fixation, vitamin production, and chemical breakdown of toxic components, such as the reduction of salts in the soil. In addition, compounds such as fertilizers, refined petroleum products, pesticides and herbicides may also be broken down into non-toxic compounds. The basic chemical and biological processes are relatively well understood, but replication of some results from the field in a laboratory environment has not been successful. We have been using these processes for treatments with repeatable success, but we are building a more complete engineering data set for field applications. Additional laboratory work is underway to understand why they work, so that the laboratory processes can be improved to seek better, more economical results in the field.

Two types of processes are used by microorganisms to transform compounds from undesirable states to desirable states. These include growth and cometabolism. Growth is the process by which microorganisms reproduce and increase in numbers. Cometabolism is a process where the microorganism uses the pollution compound as a source of carbon and/or energy, i.e. food. Often, a symbiotic relationship occurs between microorganisms where one species breaks down harmful compounds into a form that then becomes food for another species. Thus, combining multiple species of microorganisms can enhance the overall remediation process.

While research is being done to genetically alter microorganisms to achieve specific goals, we have taken the approach that by selectively growing and applying naturally existing microorganisms in an effective manner, we can achieve our goals without introducing potentially catastrophic impacts into our ecosystem. Unfortunately, the natural unamplified processes of biological remediation in the wild are relatively slow, and are limited by the species and population of microbes in each area. A concentrated spill could overwhelm the existing microbial population, or in any case, the time it would take for the natural processes to take place is not economically viable. The solution then becomes to either introduce additional microbial populations or find a way to stimulate the growth of existing populations to the point that they can positively impact the remediation process. By applying the appropriate nutrients, we can increase the growth of the microbe population to speed remediation.

In addition to removing pollutants, microorganisms can assist in restoring vitality and growth capability to soil structures. Farmers have been treating soils for many years to reduce the effects of "hardpan". The dictionary defines hardpan as a layer of soil where the soil grains are cemented together by bonding agents such as iron oxide and calcium carbonate, which forms a hard mass that interferes with the movement of moisture, oxygen, and plant roots through the soil. Photo 1 shows a sample of hardpan from a site in West Texas.

In the 1950's, processes were developed that were used to enhance the growth of naturally occurring microbes by applying a culture of microbes and nutritional enzymes to an affected area. The process we have been studying has been used in over 300 individual locations, providing a rich data set for analysis. Other operators have also performed similar types of treatments. While the treatments were generally successful, differences in how the processes were executed have resulted in variances in the results and the scope of the treatment required to meet environmental standards. Often, when it is not well understood how the processes work, the operator does not know how much of a solution is required, the approach has been to use larger and larger quantities of treatment solution to achieve similar goals. This is the old oilfield approach of "using a bigger wrench". While it may work, it unnecessarily uses excess time and materials to achieve what could be done more economically.

This paper documents the work that has been done, and assesses the results of the treatments to correlate features and techniques that enhanced or diminished success rates. This analysis was then used to engineer processes to maximize the consistency of results at minimum cost.

The first step in the engineering process is to identify and accumulate sufficient quantities of the appropriate microbes to be able to effect treatment. By turning to the science of agriculture, we find that the farming community has used biological treatments for many years to treat soils to remediate and enhance farm production. There are numerous suppliers that grow and provide solutions of microorganisms that are useful in remediating hydrocarbons and Chlorides.

The second approach is to identify compounds or additives that will enhance the growth of desired microbes. One method is to apply organic material to the soil, which provides an increased food source for existing microbial populations as well as the necessary nutrition for microbes introduced to the soil as part of the treatment regime. A good example of this is using a compost pile to process household waste for use in your home garden. We have simply scaled up the process. We have also investigated and identified compounds and additives that enhance microbe growth when added to the soil structure.

The third approach is to improve the effectiveness of the application of the solution of microorganisms and take actions that will promote their activity in the remediation process. Treatment in a random fashion may result in inadequate treatment or excessive costs due to the application of treatment volumes more than the minimum required to achieve results. It is important to deliver the treatment solutions to a sufficient ground depth so that remediation can occur. We have determined that the process of injecting the solution can also contribute to success by disturbing the soil and exposing more soil to the treatment solution and to environmental oxygen.

We have developed specialized equipment intended to standardize the processes to achieve higher efficiency and uniformity of results. The new equipment delivers the solutions so that adequate ground penetration is achieved, flow is directed and concentrated in desired areas, and sensors are used to determine the areal extent of coverage and depth of penetration in the soil as the soil is mixed and disturbed in the process. In addition, where feasible, the processes are enhanced by turning the soil using traditional farming equipment such as rakes, disks, and plows, exposing more of the soil to sources of oxygen and sunlight. Depending on the needs of the situation, the processes can be engineered to add additional oxygen by injecting oxygen rich compounds such as calcium peroxide or hydrogen peroxide.

Six treatments are described in this paper as representative examples of the effectiveness of the process. Soil samples were taken before and after the treatments. Depending on the location, different laboratories performed the analysis, but the tests were performed in accordance with EPA and Texas Commission on Environmental Quality (TCEQ) standards. Depending on the nature of the spill, the samples were analyzed for Chlorides and hydrocarbon contamination. Samples were taken both at the surface and at a depth of 12" to determine the effect of contaminant migration through the soil, and the effectiveness of the treatment regimen.

Appendix 1 contains photos that were obtained at two sites which demonstrate physical evidence of the efficacy of the treatment processes.

Site 1 – Near Garden City, Texas

The first treatment reviewed involved the remediation of a wellsite in West Texas near Garden City, Texas[1]. A pretreatment soil sample was taken at one site at the surface and at a depth of 12". The soil samples were chemically analyzed by a commercial laboratory for Chlorides only. The surface sample indicated a Chloride level of 29,400 mg/Kg, and the 12" depth sample indicated a Chloride level of 23,200 mg/Kg, which suggests that the contamination was not only present at the surface, but had migrated to a depth of at least 12".

The site was treated as described above and samples were taken 19 days after the treatment at the surface and at a depth of 12". The posttreatment analysis at the surface indicated a Chloride level below 20 mg/ Kg, or a reduction in contamination of 99.93%, and for the 12" sample, Chloride level was reduced to 3790 mg/KG or a reduction of 83.66%.

Site 2 – Near Garden City, Texas

The second treatment reviewed was completed on a site near Garden City, Texas[2], where a produced water spill had contaminated fields that were used to grow cotton. A series of four sets of samples were taken at the surface and at a depth of 12". In this case, samples were analyzed for Chlorides and hydrocarbon components.

Table 1 shows the results of the analyses of four sets of samples taken prior to the treatment

Table 1—Garden City, Texas – Before Treatment

Sample	Description	Matrix	Chloride	C6-C12	>C12-C35
1	Surface	Soil	6600	1470	13100
1	12"	Soil	<20.0	<50.0	<50.0
2	Surface	Soil	7640	1290	42200
2	12"	Soil	6600	353	1040
3	Surface	Soil	377	1300	25400
3	12"	Soil	<20.0	112	625
4	Surface	Soil	94	<50.0	<50.0
4	12	Soil	5470	<50.0	<50.0

The site was treated as described above and samples were taken after 7 days at the surface and at a depth of 12". In this case, the samples were analyzed for Chlorides only. Table 2 shows the results of the analyses of four sets of samples taken 7 days after the treatment. In addition, control samples were taken at a non- contaminated location to ensure that the base contamination of the soil was not a factor.

Table 2—Garden City, Texas - After Treatment

Sample	Description	Matrix	Measured Chloride	Reduction	C6-C12	Reduction	>C12-C35	Reduction
1	Surface	soil	2.17	100%	ND	100%	<5.00	99.96%
1	12"	soil	2.9	86%	ND	100%	<5.00	90.00%
2	Surface	soil	22	100%	109		109	99.99%
2	12"	soil	69	99%			ND	99.52%
3	Surface	soil	109	71%	ND	100%	1150	99.98%
3	12"	soil	126	N/A			ND	99.20%
4	Surface	soil	12.1	79%	ND	100%	ND	100.00%
4	12"	soil	3.35	100%	ND	100%	ND	100.00%

Reduction of crops. contaminants at this site was over 99%, and the site is now producing significant cotton crops.

Site 3 – Fisher County, Texas

The third treatment reviewed was a site in Fisher County, TX [3], where a spill contaminated a pond on the site. Water samples were taken at four points at the site, and a control sample was taken from a pond with no known contamination pond. Additionally, a soil sample was taken at the site of the rupture. Table 3 summarizes the before treatment sample results.

Table 3—Fisher County, Texas - Before Treatment

Sample	Description	Matrix	Measured Chloride	C6-C12	>C12-C35
1	Control	water	31.5	-	-
2	Rupture Site	water	94300	-	<50.0
3	Rupture Site Surface	soil	5410	<50.0	261
4	Entry Point	water	262	-	-
5	Collection Point	water	3790	<5.00	<5.00
6	Entry Point/TPH	water	-	926	45500

Contamination fluids were removed using a vacuum truck, and the contaminated soil and the pond surface were treated using the methods described above. After a week, the site was sampled again to evaluate the effectiveness of the treatment. Table 4 shows the analysis results for those samples.

Table 4—Fisher County, Texas – After Treatment

Sample	Description	Matrix	Measured Chlorides	Reduction	Extended Analysis C6-12	Reduction	Extended Analysis >C12-C35	Reduction
1	Rupture Site	soil	865	84.011%				
2	Entry Point	water	111	57.634%				
3	Collection Point/TPH	water			<5.00		<5.00	
4	Entry Point/TPH	water			<5.00	99.46%	<5.00	99.99%
5	Pond Collection	water	96.5					

Site 4 – East Texas

The fourth treatment reviewed involves a site in East Texas[4] that experienced a produced water spill in April 2016. The site was a tank battery location. Samples were taken at two locations within the spill boundary, at the surface, and also at a depth of 12 inches. These samples were then analyzed using standard testing procedures. The initial contamination of the soil was tested to be 30,000 PPM. The area was then treated using the process described above, including a biological agent. Within twenty-one days, the salt level in the soil had been reduced to 900 PPM. Local plant life was observed to be growing in the formerly contaminated soil within twenty-eight days.

Site 5 – Fisher County, Texas

The fifth treatment reviewed involves a site in West Texas[5] that experienced a produced water spill in October, 2016. The site was a pipeline used to transport produced water for collection and disposal. Samples were taken in three locations at depths of 48" and 60" to evaluate the penetration of the spilled fluids. These samples were then analyzed using EPA standard testing procedures 300 and 300.1.

Table 5—Fisher County, Texas – After Treatment

Sample	Description	Matrix	Measured Chlorides	Reduction	Extended Analysis C6-12	Reduction	Extended Analysis >C12-C35	Reduction
1	Rupture Site	soil	865	84.011%				
2	Entry Point	water	111	57.634%				
3	Collection Point/TPH	water			<5.00		<5.00	
4	Entry Point/TPH	water			<5.00	99.46%	<5.00	99.99%
5	Pond Collection	water	96.5					

Site 6 – Jal, New Mexico

Site 6 involved the treatment of a municipal sewage treatment plant in Jal, New Mexico[6]. In this incident, approximately 3000 gallons of crude oil was spilled into a storm sewer approximately 3 blocks from a lift station. The oil was pumped into an aeration lagoon and chlorine contact chamber before the spill was discovered. Testing was performed to determine the level of contamination before the treatment. During the treatment, approximately 100 gallons of treatment agent was pumped into the sewer line at the manhole above the point of contamination, approximately 40 gallons was introduced into the system at the lift station, and approximately 260 gallons was spray applied to the aeration lagoon and chlorine chamber. For a period of one month, 3 gallons of treatment agent was added daily at the manhole on the sewer line. After two months, the system was tested again to evaluate the effectiveness of the treatment process. Table 6 shows the results of testing performed before and after the treatment.

Table 6—Jal, New Mexico – Sewage Treatment Plant

Before Treatment				After Treatment			
Benzene	Ethyl Benzene	Toluene	Total Petroleum Hydrocarbons	Benzene	Ethyl Benzene	Toluene	Total Petroleum Hydrocarbons
<5.0 mg/L	1200 mg/L	270 mg/L	3300 mg/L	<5.0 mg/L	<5.0 mg/L	<5.0 mg/L	140 mg/L
Reduction →				N/A	99.58%	98.15%	99.85%

Spike Testing

To confirm the testing validity, a process called spike testing is used. In the spike process, a sample is tested, then known contaminants are added. The sample is tested again to determine the level of contaminants. This process confirms the testing and analysis procedure by adding known quantities of contamination to a clean sample, then testing to see if the results match the predicted outcomes. The results from two spike tests are shown. in Table 7.

Table 7—Spike Testing

		Sample Result	Spike Added	Sample Result	Spike Added	Sample Result
Blank Spike	Fluid	<5.00	250	275	250	268
Matrix Spike	Soil	30900	12500	48500	12500	47700

Summary

We have described a process that has been successfully used to treat hydrocarbon and produced water spills in the natural environment using fluids containing microbial agents under a wide range of conditions. The five examples described above are a representative sample of the results we have obtained, but we have completed hundreds of treatments with similar levels of success. These treatments were performed using equipment we designed and built to enhance the processes, and using techniques that we developed through years of experience. We treat the environment with what is already in the environment. These processes have applicability far beyond just the petroleum industry, and can be applied in a wide range of circumstances and environmental situations. The potential exists to be able to remediate sites that have previously been considered too difficult to attempt. The processes described in this paper offer a significant benefit not only to the oil and gas producing community, but also to the general public in that the ability to restore previously damaged soil enhances the environment we live and work in.

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Appendix 1 Example Photos

The following are photos taken at actual sites.
Cotton Field in West Texas - This spill was approximately 1200 Bbl, with no recovery. The before treatment view is from just outside the tank battery looking along the direction of spill flow down the furrows.

View from a spill site of 1200 Bbl (no recovery), prior to treatment

This picture was taken from the far extent of the spill, looking back toward the tank battery. The soil was treated, a cotton crop was planted, and has developed strong growth at this point.

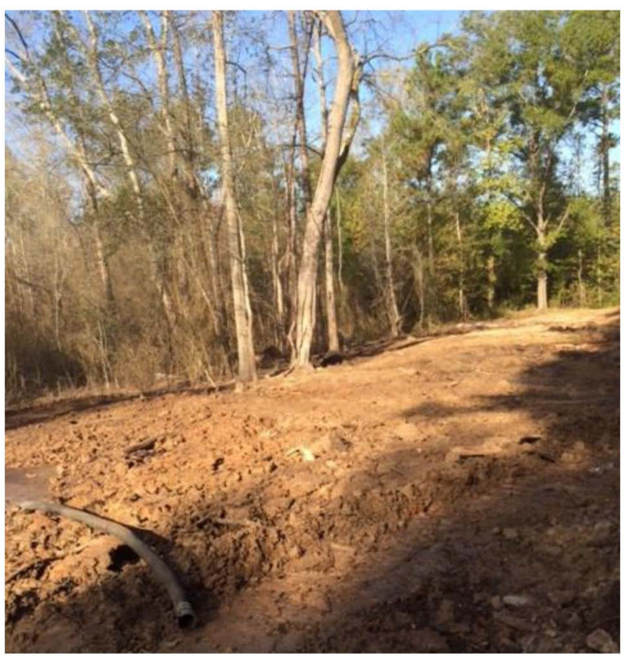
View toward tank battery after restoration and new crop planting

Crude Oil Spill near Kilgore

The following pictures are from a crude oil spill in East Texas near Kilgore, Texas. The first photo is before treatment.

Crude oil spill near Kilgore – before treatment

The following photo is the same location after remediation. For reference purposes, note the two trees in the center of the pictures.



Crude oil spill near Kilgore – after treatment