

## ©Remediation of Free Phase NAPL at A Sub-Tropical Marine Terminal Employing a Controlled In-Situ Chemical Oxidation Process (CISCOP™)

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### Summary:

A former marine liquid bulk terminal built to receive, store, and trans-ship industrial solvents by barge, rail and motor carrier was sold. Under the terms of the agreement the seller was obligated to remediate the site of petroleum derived hydrocarbon solvents present in the soil and groundwater. Because of the high concentrations of contaminants across a broad area of the site, a remedy was implemented that called for the soil above the groundwater table to be excavated and landfilled off site. However, because of the unexpectedly high mass of free phase NAPL the excavated soils were rejected thus, necessitating on-site modification prior to shipment.

A newly developed in-situ chemical oxidation (ISCO) process was employed to treat the open excavation prior to backfilling with clean soil. This step destroyed residual free phase NAPL, eliminated odors by oxidizing the odorous compounds, protected the clean backfill material from contamination by residual free phase products seeping into the excavation and provided an environment conducive to accelerated bio attenuation.

Upon completion of the excavation work, additional reagent was injected employing direct push technology (DPT) to address deeper residual soil and groundwater issues. The injection process was exploited to reveal residual contaminant sources located deeper than the extent of the excavation. This site characterization step was possible due to *the generation of small quantities of carbon dioxide gas that cause the formation of foam on the surface at the point of injection when the probe is withdrawn. Because this phenomenon occurs only where smeared or free phase NAPLs are present, it can be exploited as a contaminant location tool.* Once the sources are located the oxidizer can be pin-pointed to these areas thus, effecting a more efficient application of the oxidizer.

*Although toluene was the contaminant of concern at the site, the photographs included will reveal that a substantial mass of NAPL was present in the excavations after soil removal.* All NAPL contaminants, present on the groundwater, were mitigated by the spray application of oxidizer directly to the surface of the liquid fraction during excavation. Deeper contaminants (to eighteen (18) feet) were treated utilizing DPT rigs. *Within nine (9) months of the completion of the excavation activities, all signs of free phase product had disappeared. After one (1) year, the deeper contaminant (toluene) had been reduced to concentrations below Maximum Contaminant Levels (MCL) required for closure. Following the required monitoring period, the site was declared closed.* Although expected, no additional ISCO applications were required. *It has subsequently been determined at numerous other sites, that where excavation activities include Cool-Ox® application prior to backfilling, aggressive and sustained biodegradation occurs.* Rapid shrinkage of the contaminated groundwater plume follows the elimination of the contaminant sources.

## Remediation History:

The pictures in this report will reveal that there were numerous challenges posed at this former bulk liquid marine terminal. Time was a significant limiting factor in the selection of remedial processes because the aggressive building construction schedule imposed by the new owner limited the technologies that could be used for clean-up. ***Although excavation was selected as the primary method to remove the bulk of the contaminated soil, excavation could not accomplish mitigation of contaminants in the saturated zone nor (as it was discovered at the on-set of the excavation work) the capillary fringe.*** Thus, a combination of excavation supplemented by chemical oxidation was selected. This report will present an overview of the project and the significant variations to the original work plan necessary to address the unexpected conditions encountered during the excavation work. A photographic record is also presented with brief explanations to provide the reader with a pictorial insight into the challenges encountered and how they were overcome.

During the characterization phase of the project, free phase product was discovered in several areas of the site. Although product recovery systems might have extracted a portion of this material, the decision was made to excavate the contaminated soil down to the water table (approximately five (5) feet) over the entire two and one half (2½) acre site to accommodate the new owner's aggressive construction schedule. The excavation work was accomplished by excavating plots of approximately twenty (20) to thirty (30) foot squares and backfilling each plot with clean soil prior to excavating the next cell. ***Several valid reasons were taken into account to combine ISCO with the excavation work which justified this approach including, the capability of the oxidation reagent to quench odors generated by the aromatic hydrocarbons.*** Excavation, although meeting the majority of the criteria of the remedial design, had one serious flaw. Specifically, ***as the contaminated soil was excavated free product present at the soil/groundwater interface in the unexcavated area, seeped into the excavation and thus, contaminated the clean backfill as it was placed.*** The capillary action of the clean fill material wicked the free phase products like a sponge thus, defeating the remediation objective of the project. This problem was solved by spraying the excavation with the oxidizing Technology developed and patented by William Lundy. This technology became known as the *Cool-Ox*<sup>®</sup> Process.



Photo 1

Photo 1 depicts the northeast corner of the terminal as it appeared prior to excavation activities. This placid scene belies an area of some of the highest contaminant concentrations on the site.



Photo 2

Casual water collected in the treatment area during a rain storm typical of the climate.

**Events:** Once excavation began, it was discovered that the contaminated soil, intended to be land-filled, did not meet acceptance specifications at the facility. This discovery required that two immediate revisions be made to the project work plan. The first, required locating an alternative disposal facility that held the proper permits to accept the heavily contaminated soil. The second significantly increased the quantity of the *Cool-Ox*<sup>®</sup> reagent needed to meet the oxidation demands posed by the increased contaminant

mass. Although at the time, these changes were viewed as an unexpected and certainly unwelcome expense, they actually resulted in a substantial cost savings to the project.

*The most significant challenge of any in-situ technology (including chemical oxidation) that requires contact between the reagent and the contaminant, is the ability to “wet” the target pollutant with the remedial compound.* This problem is far more complicated with oxidation mechanisms (where the viability of the reagent expires over a relatively short period of time), than with biological processes where the microbes can essentially “lay in wait” for a passing meal. Therefore, *the mixing of the pollutants with the oxidation reagent was vital to the success of the cleanup.* It was discovered (fortunately, during the early hours of the project) that *the agitation of the contaminated groundwater caused by the aggressive spray action of the application followed by the turbulence caused by the placement of the backfill, fulfilled this need with a high degree of efficiency.*



Photo 3

Photo 3 depicts casual water, carrying contaminants, mixing with the pretreated water in the pit. The heavy foam indicative of the reaction of the contaminants with the *Cool-Ox*<sup>®</sup> reagent can be seen in the foreground. A marked decline in odor was also observed after mixing.

At the start of the project, a test pit was excavated to assess the effect of the reagent on the contaminants remaining in the void and to address the seepage of these pollutants borne by the groundwater. The expected foaming occurred when the reagent contacted the contaminant

on the surface of the water and a noticeable decline in odors was immediately apparent. The application was conducted Friday afternoon and the excavation was left open over the weekend. **Observation of the pit the following Monday revealed that the water was free of any sheen or odor and appeared to be relatively clear (transparent).** This result was expected. However, a subsequent event demonstrated the technology to be far more effective than previously observed.



Photo 4 depicts free product encountered along the north edge of the excavation area. The depth of product was approximately 1/2 inch.

a heavy foam reaction was observed as the treated water was agitated by the incoming flow water, indicating that the reagent applied to the excavation three (3) days earlier was still viable; and secondly, **as the foam spread over the surface of the water, a decided suppression of odor (indicative of aromatics) occurred.**

The results of the reactions that took place (as shown in Photo 3) **demonstrated clearly that the agitation produced by the mixing of the casual water with the groundwater (and in later observations, the backfill soil with the water in the excavations) contributed significantly to the oxidation reactions.** Once it was determined that the placement of the backfill produced sufficient agitation between the reagent and the free product to facilitate satisfactory mixing (thus contaminant destruction), **a significant cost savings was**



Photo 5 depicts the typical over-spray application method used to treat excavations. A formulation slightly more aggressive than the *Cool-Ox*<sup>®</sup> in-situ reagent is used for excavations. This formulation is trademarked *Pit-Stop*<sup>™</sup>. Both are applied with DTI's *Deep-Shot*<sup>™</sup> Rig.

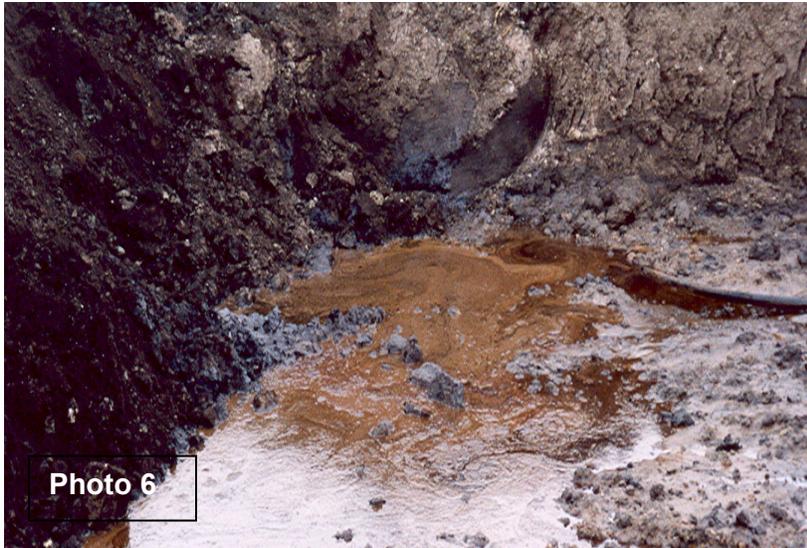


Photo 6

Photo 6 shows free product reacting with *Cool-Ox*<sup>®</sup> reagent. As the reaction proceeds the color shifts from the dark brown of the contaminant to a tan. DTI uses this color change as an indicator to monitor the activity of the oxidation reaction. ***A combination of the generation of carbon dioxide and the hydroxylation of the hydrocarbon (surfactant production) creates a stiff foam signaling the oxidative destruction of contaminants.*** It is very important to note that although a tight lather is formed by this reaction, no heat is generated. Thus thermal volatilization is obviated.

It should also be noted that prior to application, the surface tension of the groundwater at most sites is usually quite constant at approximately 74 dynes/cm. This value drops to circa 34 dynes/cm within minutes after application of the oxidizer. This drop in surface tension is indicative of the conversion of the contaminants to surfactants as they are hydroxylated by the oxidation reactions. Thus, the VOCs are not only sequestered by the formation of the foam on the surface of the groundwater but, are themselves, actually converted to a new, more water soluble molecule. ***In summary, it is important to understand that the technology does not trap the odor bodies as is the case with the use of commercial foam products; but, instead oxidizes them so that they become part of the foam blanket composed of oxidized contaminants.***

***realized by this modification in the project design.*** This, excavate/spray & application/backfill, procedure was continued over the entire two and one-half (2½) acre site. ***The ability to destroy a significant mass of contaminants employing this over-spray method also had a vitally important serendipitous affect on the subsequent injection events.***

The original injection design called for injection points (IPs) to be spaced using a five (5) foot matrix. However, because of the much greater than expected destruction of contaminant mass enjoyed from the overspray mixing capability, the injection matrix was increased to seven (7) feet. This change was very significant in that, at the five foot matrix, the number of points was nearly double that of the seven foot matrix. Therefore, adopting a seven foot matrix allowed for a large expansion of the area to be treated by injection and thus increased the probability of success because the reagent was distributed over a much broader area. However, the larger than expected increases in the areas as well as quantities of free product encountered during the

excavation work underpinned previous conclusions that ***removal of the soil contaminants (NAPL) must be accomplished before the groundwater could be mitigated.*** The following series of photos depict the widespread free product encountered during the excavation activities.



Photo 7

Photo 7 depicts an excavation where almost all of the LNAPL in the excavation has reacted with the *Cool-Ox*<sup>®</sup> reagent. Only the dark area (see arrow) reveals traces of the contaminant. Note the heavy lather covering the groundwater forms a barrier that prevents the escape of odorous volatile compounds.

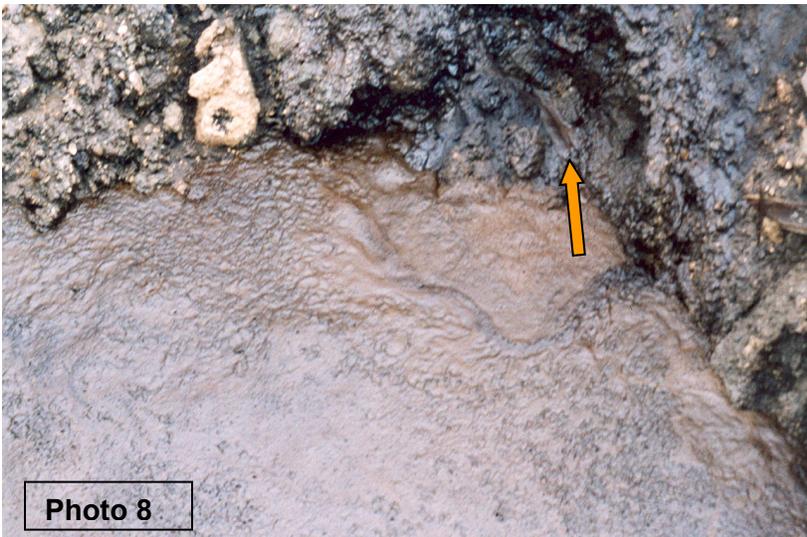


Photo 8

Photo 8 depicts heavy reactions reducing the mass of free product. The *Cool-Ox*<sup>®</sup> process has two significant advantages over conventional chemical oxidation processes. First, the process does not produce heat so that thermal volatilization does not occur. Secondly, because the reaction is overt, the trained observer can apply additional reagent to the excavation if it is apparent that more is needed. The dark area (arrow) at the top reveals a migration pathway where the contaminant was pooled.

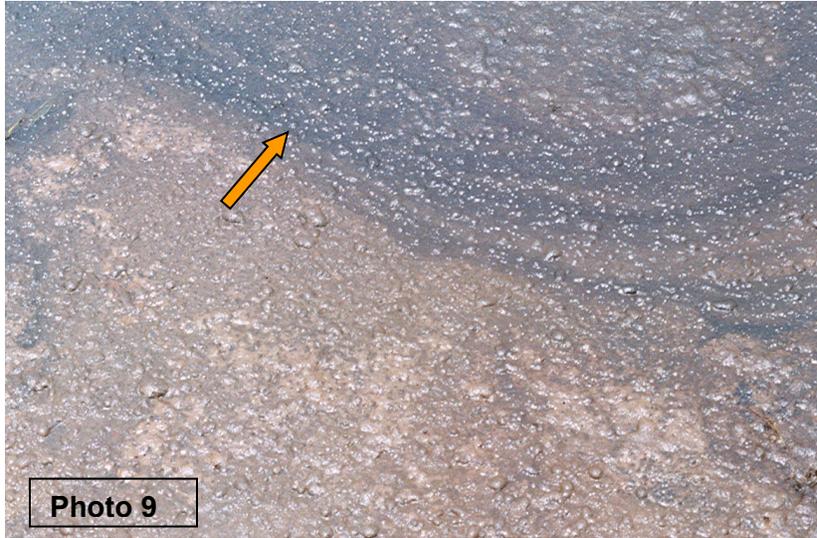


Photo 9 was taken near the center of an excavation where NAPL had intruded to cover the ground to a depth of approximately ½ inch. Note the lines and heavier concentrations (arrow) of product in the upper portion of the photo.

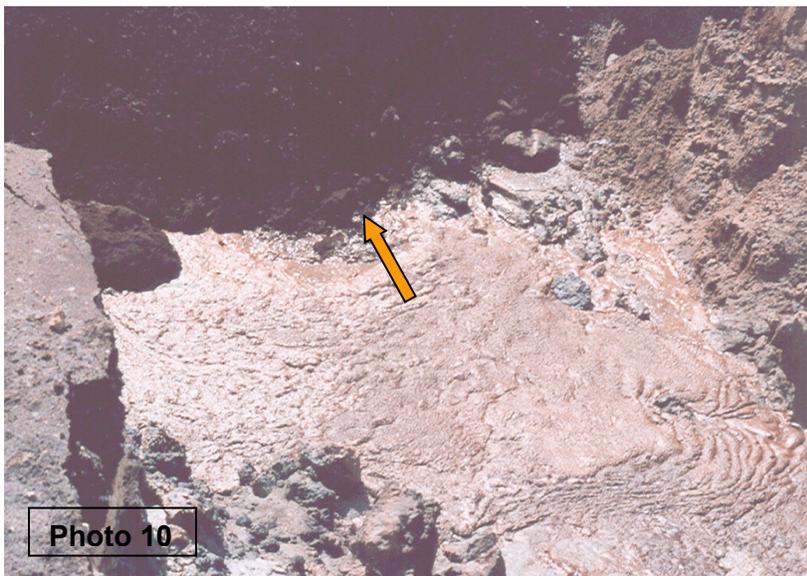


Photo 10 reveals backfill material (dark soil at the top of the photo – see arrow) causing agitation of reagent and contaminant of the water in the excavation. Note the tan color of the foam indicating oxidation.



Photo 11 depicts groundwater and treated product oozing up (arrow) under weight of excavation equipment. This picture is significant because it shows that if reagent were not applied, the backfill material may eventually also require excavation.



Photo 12 depicts an old wooden foundation uncovered during the excavation. Note the contaminant reacting with the oxidizer in the foreground (arrow).



Photo 13 depicts free phase NAPL discovered north of the old wooden foundation. This is a significant discovery because this test excavation is located outside of the designed excavation area where the *Cool-Ox*® application was truncated. Treatment of the contaminant in this area was accomplished only by injection of the oxidizer employing direct push equipment.



Photo 14 shows two Direct Push Technology (DPT) rigs at work treating deep contaminants through the clean backfill after the excavation work was complete. Both rigs are supplied by a single pump unit.

Upon completion of the excavation activities, injection work using direct push equipment was conducted to treat the vertical extent of the contaminant zone extending below the water table. *Injection applications have proven very successful in remediating sources where the contaminants are located below the groundwater table or where the depth precludes excavation.*

This technology is also useful in locating sources of hydrocarbons where the contaminants are either perched or present in concentrated smear zones. This phenomenon is very useful in locating sources quickly, and is a good indicator of what might be expected in groundwater analytical results. At sites with no source areas or in down-gradient contaminated groundwater plumes,

results are usually immediate or observed within the period of time normal to accelerated microbial proliferation. Because of the very high concentration of soil contamination found at this site, it was anticipated that additional groundwater applications would be required. However, subsequent sampling data revealed that additional applications were not necessary. This was attributed to the fact that although a significant mass of free phase NAPL remained in the excavation after the



Not all days were easy. Photo 15 shows the advantage of the DPT crawler under very wet conditions.

contaminated soil was removed, it was directly exposed to the *Cool-Ox*<sup>®</sup> reagent. Thus, *the agitation caused by the direct forceful spraying of the oxidizer coupled with turbulence caused by the backfilling activity facilitated maximum contact between the contaminant and oxidizer.*



Photo 16 locating a heavily contaminated hot spot. Not a welcome site. However finding the sources is a must if they are to be eliminated. This is the first step to mitigation of groundwater. Note the lather at the periphery of the surface reaction as the *Cool-Ox*<sup>®</sup> reagent reacts with the product.

Post treatment groundwater data indicated that the highest concentrations of contaminants in the groundwater were in areas where the greatest volumes of free product were observed during the *Cool-Ox*<sup>®</sup> application. With the exception of only two areas, the data also revealed that the concentrations of toluene (the target pollutant) were all below site closure levels. It was also determined that the *free product had been eliminated by the combination of excavation and subsequent chemical oxidation treatment*. These results indicated that *as the contaminant mass in the soil is mitigated, significant decreases in the groundwater concentrations could be expected from the oxidation phase as well as accelerated biodegradation subsequent to the oxidation event*.

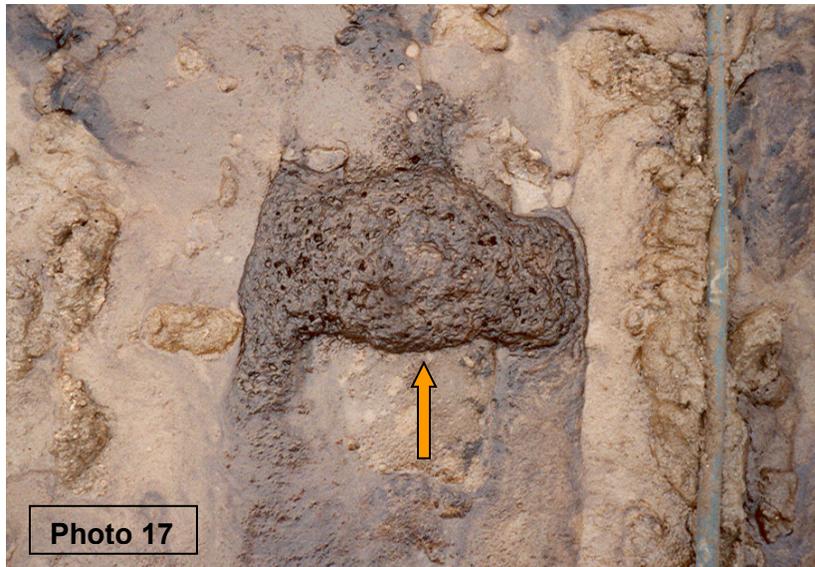


Photo 17 depicts the discovery of a “hot spot.” As the injection tooling is withdrawn, free product is reflected to the surface (arrow) by the reaction of the *Cool-Ox*<sup>®</sup> reagent with pooled contaminant. This reaction has been used to locate product at service stations, industrial sites, pipelines, railroads and at this marine terminal. It should be noted that the ability of the oxidizer to locate contaminant sources allows these areas to be vigorously treated and is one of the primary factors in the elimination of the NAPL. This characterization phenomenon and the longevity of active oxidizer (up to 90 & 120 days) combine to ultimately eradicate the NAPL.

At this point, an extremely important point must be made. That is, *if the soil becomes saturated before the quantity of reagent necessary for destruction of the contaminant mass can be injected, additional application(s) will be necessary*.

Although only toluene was identified as the target pollutant, other hydrocarbon co-contaminants were observed during the excavation work. If co-contaminants are present in substantial concentrations, they will produce a significant oxidizer demand. This should always be considered in the designed remedy. However, even these more viscous, heavier hydrocarbons were remediated, leaving only “hot spots” in the groundwater for further attention. DTI has determined that this is quite normal in the majority of sites treated. The general rule is that *the soil sources must be eliminated before the groundwater can be mitigated*.



Photo 18 is a composite photo depicting free phase product reflected to the surface (orange arrow). At right, the photo (taken approximately 5 minutes later, (green arrow) shows the product dissipating as it is hydroxylated by the *Cool-Ox*<sup>®</sup> reaction. Moments later as the oxidation reaction proceeded, the product was converted to stiff foam resembling that shown in Photo 17.



**Photo 19**

Photo 19 reveals the natural (bleached clean) color of the soil on the final day of operations. Orange utility flags show the locations of injection points. Although it was expected that additional *Cool-Ox*<sup>®</sup> applications would be required, the combination of direct over-spray to open excavations coupled with the aggressive in-situ treatment of source areas revealed by the technology, proved sufficient to achieve closure. Shortly after completion of the remedial work a base layer of aggregate was applied to prepare the site for construction work.



**Photo 20**

Early morning at the terminal.

## Summary:

This former marine terminal presented an interesting and diverse set of challenges.

- 1) It was the first time the *Cool-Ox*<sup>®</sup> process had been used on a large scale to treat excavated areas in an effort to directly treat exposed contaminants and protect backfill soil from recontamination. Given the apparent reductions in the concentrations of the contaminants remaining in the groundwater after treatment and the oxidation effect on the contaminants unearthed during excavation work as depicted in the photos presented in this report, the Technology performed very well.
- 2) The photographic record reveals that the mass of contaminants encountered during the *Cool-Ox*<sup>®</sup> application included a much broader spectrum of products than just toluene. Visual inspection of the free phase product on the groundwater in the excavations revealed the presence very large concentrations of hydrocarbons more viscous than toluene. To determine the true extent of the effect of the technology on the reduction of mass, total petroleum hydrocarbon (TPH) data is necessary. Lacking this data, if one compares the concentrations of toluene prior to application with the post treatment concentrations, it would appear that the total reduction of mass was significant.
- 3) A second very important conclusion can be drawn from the presence of oily/waxy (paraffinic) hydrocarbons at the site. These contaminants accumulate at the surface of the groundwater and adsorb to soil. As the groundwater level fluctuates, these paraffinic hydrocarbons are adsorbed over a vertical interval at the capillary fringe. This zone of adsorbed contaminants is referred to as the “smear zone” and is the location of the source of almost all target pollutants. Heavier hydrocarbons (diesel fuel range or greater) are more paraffinic in nature and as such adsorb to soil to form a tight matrix structure often resembling a block of very dirty lower molecular weight wax. Because volatile organic compounds (VOCs), (SVOCs), as well as halogenated organics are infinitely soluble in this hydrophobic structure, they are released into the groundwater (where by comparison, they are nearly insoluble) at a rate below their coefficient of solubility. Thus, conventional remedial systems such as soil vapor extraction (SVE) or product recovery systems are for the most part obviated particularly, when the contaminants are bound in a clay soil matrix. This project has demonstrated that *Cool-Ox*<sup>®</sup> Technology is a very versatile and effective remedial technology to address this type of hydrocarbon contaminant problem.
- 4) In all aspects, the technology performed as expected and in the excavation over-spray application, performance was better than anticipated.
- 5) The post treatment reductions of toluene concentrations in groundwater were significant. An overall 90% reduction in contaminant mass was achieved. It is concluded these reductions were aided by the increased mixing from agitation caused by the aggressive spray activity and backfilling.
- 6) Applications at other sites coupled with results enjoyed at this project revealed that the chemistry can successfully destroy the contaminants. Application technique to improve contact between the oxidizer and contaminant remains a very significant component of in-situ work.
- 7) Under the circumstances found at this terminal (soil types, contaminant species, most opportune biological mechanisms for these contaminants, warm climate, etc.), it became

apparent that the *Cool-Ox*<sup>®</sup> technology was well suited as a long-term remedy to address soil and groundwater impacts.

8) Some “hot spot” free product areas remained after the excavation activities. The ability of the technology to locate these sources was demonstrated during the site work. Once the hot spots were located, additional reagent was applied to specifically target these areas.

9) Post treatment sampling data revealed that the nutrients inherent in buffering the *Cool-Ox*<sup>®</sup> formulation, combined with excess oxygen produce, and the carbon source available from partially oxidized (now biodegradable) contaminants; combined to stimulate the activity and proliferation of natural intrinsic microbes. Thus, biodegradation became a major component of the remedy. This continuing long-term phenomenon created a decreasing trend in groundwater contaminant concentrations that has been observed at other sites as well. No laboratory produced bacteria were applied

10) Subsequent to application, contaminant concentrations reached closure levels in approximately twenty-four (24) months. The site was then placed in the Monitored Natural Attenuation Program as a candidate for No Further Action. It has since closed.

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