USING CHEMICAL OXIDATION TO DELINEATE A CONTAMINATE PLUME FROM A PIPELINE RELEASE

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Introduction

Because conventional plume delineation techniques had failed to locate the boundaries of a hydrocarbon soil plume caused by a pipeline release, a controlled in-situ chemical oxidation (ISCO) process was evaluated to assess its usefulness as a forensic tool to locate and delineate in-situ contaminants.

Project Background

The subject site is identified as an alfalfa field located in rural Illinois. The pipeline operator maintains one (1) twenty-four (24) inch diameter petroleum product pipeline in an approximate north-south orientation in the site vicinity. The petroleum pipeline was installed in 1971, at a depth of approximately seven (7) feet below grade surface (bgs). The line is used to transport three (3) refined petroleum products, these include unleaded gasoline, jet fuel and fuel oil. Two (2) product releases, attributed to an insulated flange failure, occurred in 1983 and 1984. Unleaded gasoline was released in both incidents, with approximately fifty (50) barrels of product recovered following the releases. Approximately three hundred (300) feet of pipeline, north from the insulated flange, was excavated and re-aligned following the second release.

Soil samples were collected from twelve (12) probe locations and groundwater was collected from ten (10) of the twelve (12) probe locations. Total petroleum hydrocarbons (TPH) concentrations in the groundwater ranged from below detection limit to 174 milligrams per Liter (mg/L). Free product was reportedly encountered in the area of the first release. Soil TPH concentrations at 4 to 5 feet (bgs) ranged from 0.0005 to 305 mg/Kg; soil TPH concentrations at 8 to 10 feet bgs ranged from 0.001 to 443 mg/Kg; and soil TPH concentrations at 12 to 15 feet bgs ranged from below reporting limits to 185 mg/Kg.

The previous consultant concluded that the petroleum hydrocarbon plume had been delineated, and that the contaminants had migrated approximately 450 feet south, 150 feet west, 250 feet east, and 210 feet north from the release area. It was also concluded that groundwater flow was in a "southerly" direction. Soil and groundwater analytical data were tabulated and included in a summary report.

Terracon performed limited Phase II ESA sampling on the site on February 14, 1997. Activities consisted of advancing hand auger samples at six (6) locations on the site to assess the impact to site soils. Soil samples were collected at depths ranging from 2.5 to 3.5 feet bgs. Benzene, ethylbenzene, toluene, and total xylenes concentrations exceeding regulatory guidelines were identified in three (3) of the six (6) samples submitted. Between December 28th and 30th, 1998, Terracon mobilized to the site to install seven (7) monitoring wells using an all-terrain vehicle (ATV) mounted CME drill rig.

Site Conditions

The soil at the subject site is classified as Elco silty clay loam, 5 to 10 percent slopes, severely eroded, and Marine silt loam, 2 to 5 percent slopes. Elco silty clay loam consists of silty clay and clay loam. Permeability is moderate and surface runoff is medium. The site soils are also referred to as the Hickory-Elco-Rozetta Association. The Association consists of moderately sloping to steep, well drained and moderately well drained soils that have a moderately permeable for moderately slowly permeable subsoil. The association is formed in glacial till, loess, and less over an older buried soil on uplands. The association is on narrow upland ridges and on valley side slopes, which were originally covered by deciduous forest. Subsurface soils at the site generally consisted of interbedded layers of silt, lean clay, and fat clay. Trace amounts of sand and rounded gravel were observed in several borings.

According to the Soil Survey, scattered sand and gravel aquifers in the underlying till plain provides supply wells with moderate amounts of water for small communities and rural households. Drinking water for most rural households is supplied by low-yielding wells that are 35 to 150 feet deep.

Groundwater has been encountered at depths ranging from 4.8 to 18.7 feet (bgs). Typically, the groundwater averages in the range of 12 to 14 feet bgs. The groundwater flow direction appears to be to the south/southwest, reflecting the topography, drainage pattern, and proximity to a south-trending tributary of Indian Creek, located approximately 500 feet west from the site. Subsurface and localized geologic conditions can alter normally expected flow direction. In addition, perched groundwater zones may be present.

Free Product Remediation

Enhanced Fluid Recovery (EFR) was initially used to recover the free product. EFR is an integrated approach involving three-phase flow and recovery. The process involves applying a high vacuum (approximately 26 inches of mercury) to the subsurface at a well point to create a pressure gradient toward the well. The pumping technology simultaneously extracts groundwater, separate-phase petroleum hydrocarbon, if present, and vapors from the subsurface in the same process stream. The greater the vacuum applied to the subsurface, the larger the pressure gradient achieved, and therefore, the higher the flow rates from the formation.

Vacuum is applied using a vacuum truck. The vacuum is applied at the air/water interface or in the case of shallow groundwater or small diameter well casings, at the well head. The length of time the vacuum is applied to the well varies based on field conditions. Typically, the wells are evacuated several times in one day or round. Collected fluids were transported to a recovery facility for recycling. Once the determination was made that the EFR remedial technique had reduced the free product to the point that on-going operation of the system would be ineffective, an in-situ chemical oxidation (ISCO) technology developed by William Lundy (the *Cool-Ox® Process*) was selected to "polish" the site and hopefully bring it to environmental closure. However, the injection process was canceled after free phase petroleum product (See Photo 1) was observed in two monitoring wells in the injection zone.

Photo 1 - Free Product

Upon discovery of the free product, further free product removal and delineation were conducted. Through Geoprobe assessments and EFR events, the general areal extent of the product plume has been delineated. However, there was a concern that additional perched product concentrations existed outside the effective influence of the installed wells. To address free phase product conditions on site, Terracon performed a site characterization program to delineate areas of high petroleum impact that it hoped, would encompass all perched free product zones. The forensic process selected was similar to the original proposed ISCO remediation process that was to be implemented before the discovery of free phase product.

The *Cool-Ox® Process* reagents contain oxidizers, that produce small volumes of carbon-dioxide gas when reacting with petroleum products. This reaction is a foaming of reagent slowly issuing from the injection probe hole when the injector is withdrawn (See Photo 2). The appearance of the foam (resembling dirty shaving lather) is used to determine the degree of contaminant impact at the injection location. Observing reactions from one injection point to another on a grid pattern across the site, allows the experienced practitioner to delineate areas of high contaminant impact.

The differences between the *Cool-Ox® Process* site characterization program and the remedial process originally proposed, is simply the number of injection points, their spacing, and volume of reagent delivered to the subsurface. A unique and extremely beneficial characteristic of the *Cool-Ox® Process* site diagnostic technology is that the same reagent used in both the forensic and the remedial processes. Therefore, ***the process not only provides a site characterization function but, delivers in-situ site remediation at the same time.***

Photo 2: Mild off-gassing of the reagent in contact with hydrocarbons.

Injection Process

As previously stated, one of the components in the *Cool-Ox® Process* is an oxidizer. When the oxidizer contacts organic contaminants, a chemical reaction occurs. The reaction causes an effervescing, that along with its coloration, odor and appearance is used as a qualitative and quantitative indicator of potential hydrocarbon impact at that location.

The assessment/injection process was started in the known or suspected areas of high impact and proceeded outward in a crisscross type grid until observations of the chemical reaction indicated a lack of substantial contaminant impact. The depth of the injection was based on water table elevations at the time of injection. The injection depth was generally between ten (10) to fifteen (15) feet bgs. The *Cool-Ox® reagent* was prepared on site for direct injection into the soil. Direct push drilling (DPT) technology was used to inject approximately twenty (20) gallons of reagent at each injection point.

Observations

Each injection point was observed by Mr. Lundy and Terracon personnel and logged. The following characteristics were recorded;

- Relative intensity of effervescing from the injection port,
- Coloration of foam and/or observance of a petroleum type sheen,
- Olfactory characteristics and/or organic vapor readings, and;
- Comparison of characteristics to previous probes along the injection grid.

Four (4) levels of potential impact were established. Table 1 below provides details. In general, the color of the foam produced by the chemical reaction would change from a cream color to tan to brown as impact concentrations increased. If free product conditions were present, there would also be a noticeable petroleum type sheen along with the foaming reagent exiting the

probe hole. A petroleum odor was also noticeable however, the odor rapidly subsided as the contaminant was oxidized. A Thermo-Environmental Organic Vapor Meter (OVM) was used to quantify the off-gasses from the injection point as part of the evaluation process.

Each injection point was assigned a unique number and then assigned a ranking number that indicated the apparent concentration of product encountered in the soil at that particular location. Observations of the injection points are tabulated and are included as Table 1.

Table 1

Letter Designation	Impact Potential Description	Map Coloration
A	Strongest indication of free product conditions	Red
B	Good indication of potential free product conditions	Orange
C	Fair indicator of high concentrations of petroleum impact (i.e. non-free product conditions)	Yellow
D	Probable indicator of reduced concentrations of petroleum impact (i.e. approaching a remedial boundary condition)	Green

The area of each suspected contaminant concentration has also been calculated and shown Table 2 below. A site map of the designated areas in Table 2 is depicted in Figure 1. The forensic information developed using the *Cool-Ox®* technology was later verified by gathering soil samples and analyzing for the presence of hydrocarbon concentrations.

Table 2 – Estimated Square Footage

Letter Designation	Impact Potential Description	Total Area* North Side	Total Area* South Side
A	Strongest indication of free product conditions	6,800	240
B	Good indication of potential free product conditions	7,100	14,000
C	Fair indicator of high concentrations of petroleum impact (i.e. non-free product conditions)	12,150	11,300
D	Probable indicator of reduced concentrations of petroleum impact (i.e. approaching a remedial boundary condition)	10,150	18,700

*Square Feet

Conclusions & Recommendations

Based on the site activities performed, Terracon concludes the following;

- Observations indicated that a substantial area (2.05 acres) surrounding the original pipeline release has been significantly impacted with petroleum product. Based on a review of all data obtained to date, an estimated area of approximately 4.5 acres could be classified as impacted above Illinois Tier 1 levels.

- An area of approximately 7,000 square feet (sf) appears to have free product present at the soil/groundwater interface. An additional 21,200 sf indicates a high probability of the presence of free product within the substrate.

- Based on the post treatment assessment as compared to previous data and free product recovery efforts, free product pooling appears to exist both at the water table interface and within non-homogenous pockets in vadose zone soils.

- It appears that remediation of this site to Illinois TACO Tier 1 levels is not practical or economically feasible.

- Risk based closure may be feasible utilizing site specific clean-up objectives and engineering controls. The primary impediment to site closure at the time of this report is the presence of free product.

- The *Cool-Ox*® technology performed very well as an accurate and economical site characterization tool.

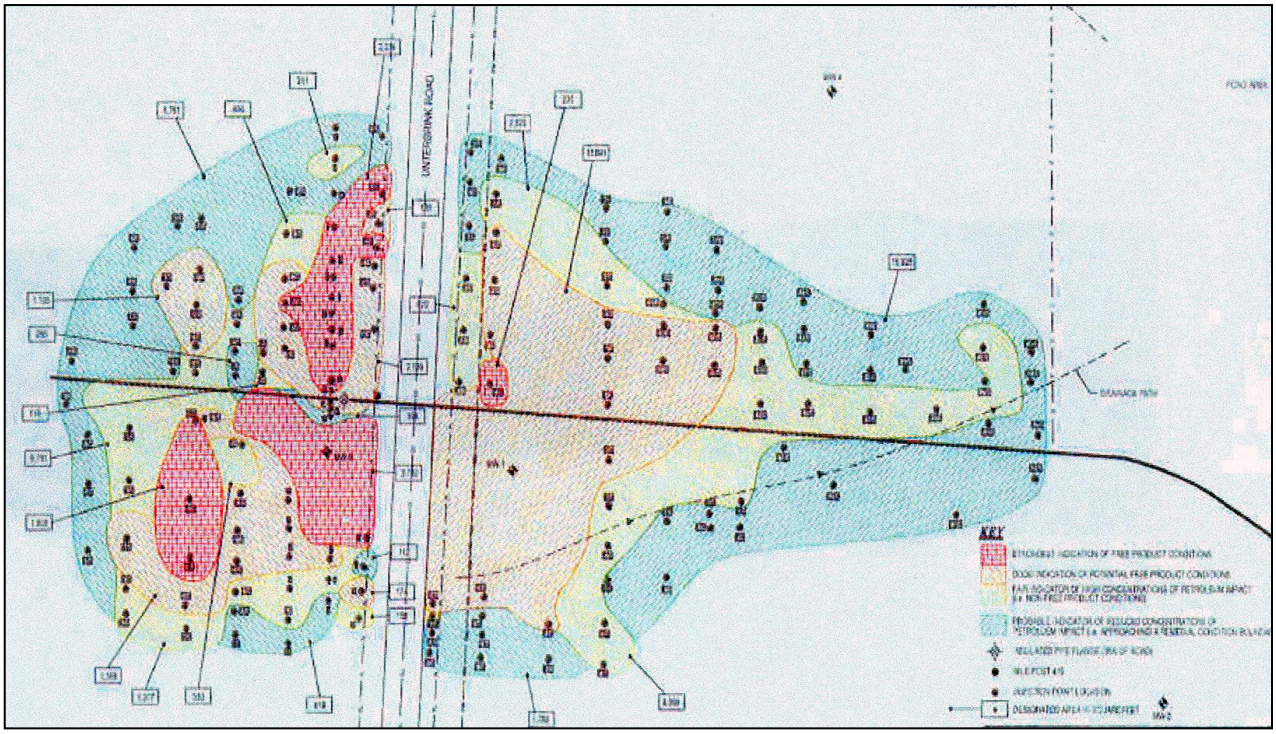

Figure 1 depicts the areas where contaminants were located