

IN SITU REMEDIATION OF VADOSE ZONE SOILS USING HYDROGEN PEROXIDE TO TREAT CHLORINATED SOLVENTS

Paul R. Stone III (USACE, Baltimore, MD)
Bryan Hoke (Letterkenny Army Depot, Chambersburg, PA)
Kenneth J. Cowan (WESTON, West Chester, PA)
Gregory S. Daloisio (WESTON, West Chester, PA)
James Wilson (Geo-Cleanse International, Inc., Kenilworth, NJ)

ABSTRACT: An innovative in situ chemical oxidation treatment technology was implemented to remediate approximately 2,150 cubic yards of vadose zone soils contaminated with F-listed chlorinated solvents at a former oil burn pit located at Letterkenny Army Depot in Chambersburg, Pennsylvania. This technology utilizes a network of controlled, pressurized injection points to destroy volatile organic compounds (VOCs) in soil by injecting a potable water solution amended with hydrogen peroxide, catalysts, and surfactants. The chemical reaction generated by this solution, originally described by Fenton (1898), creates a hydroxyl radical which is extremely effective in oxidizing complex organic compounds. The organic hydrocarbon contamination is rapidly oxidized to nonhazardous naturally occurring shorter chain mono- and di-carboxylic (fatty) acids that are further reduced by the process to carbon dioxide, oxygen, and water. A total VOC mass of approximately 5,000 pounds was present in the vadose zone soils at a depth of 5 to 23 feet below ground surface. Over 3,000 pounds of the VOC mass was composed of chlorinated solvents. The most prevalent chlorinated solvent detected was 1,1,1-trichloroethane (1,1,1-TCA) at a maximum concentration of 49,000 mg/kg. The vadose zone soils consisted of predominantly shaley to very shaley silt loams. The design of the injection system was based on the distribution of contaminants and soil permeability. Approximately 24,000 gallons of 50% hydrogen peroxide and catalyst were injected into 17 injectors over 42 days. While treating the vadose zone, the progress of the reaction was measured by monitoring the concentration of carbon dioxide off-gas from vents and nearby injectors. The carbon dioxide concentrations ranged from 10% to 20%, while the reaction was actively breaking down the contaminants and dropped to 1% to 2% as the rate of the reaction diminished. The post-injection sampling results indicate that the total VOC mass was reduced by approximately 77% while the mass of 1,1,1-TCA was reduced by approximately 83%. Because VOC concentrations remain above the generic Act 2 standards established as cleanup goals for the site, a baseline risk assessment is being conducted as part of the ongoing Remedial Investigation (RI) to see if remaining contaminants pose an unacceptable risk based on future land use. The remediation results indicate that when properly applied, this in situ remediation technology is a cost-effective alternative with rapid results that can effectively lower chlorinated solvent concentrations in vadose zone soils.

1.1 PROJECT DESCRIPTION

This soil remediation project was conducted under the direction of the United States Army Corps of Engineers (USACE), Baltimore District and the Letterkenny Army Depot BRAC Environmental Coordinator at the Letterkenny Army Depot (LEAD) in Chambersburg, Pennsylvania. The remediation project utilized an in situ chemical oxidation process to treat vadose zone soils that would require classification as F-listed hazardous waste if excavated for disposal. The objective of the project was to reduce the concentration of select soil volatile organic compounds (VOCs) to meet the Pennsylvania Department of Environmental Protection's - Soil to Groundwater Generic Values for Non-Residential Used Aquifers with Total Dissolved Solids of $\leq 2,500$ (Act 2, Land Recycling Act, 16 August 1997).

1.2 SITE DESCRIPTION

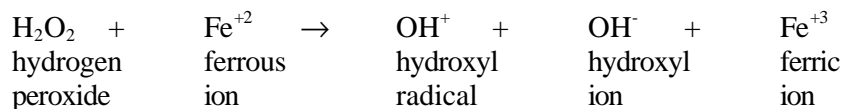
The site was an unlined former Oil Burn Pit (OBP) that was used for fire training and the disposal of waste oil and solvents in the 1970s. Soils at the OBP contained high chlorinated VOC concentrations. The highest chlorinated VOC concentrations were detected in the former surface soils. These surface soils were buried by approximately 3 to 4 feet of clean fill material that was used to backfill the OBP in order to enable a drill rig to maneuver across the site during the investigation and installation of the injection system. These former surface soils contained high organic vapor monitor readings; an area of black, oily stained soil; and a maximum 1,1,1-trichloroethane (1,1,1-TCA) concentration of 49,000 mg/kg and a total VOC concentration of 68,900 mg/kg. The soil below this former surface zone to bedrock, which was approximately 23 feet below ground surface, contained total VOC concentrations between 1,000 mg/kg and 10,000 mg/kg. The physical characteristics of the soil targeted for remediation was mostly uniform and consisted of predominantly shaley to very shaley silt loam soils with some sand lenses.

1.3 DESCRIPTION OF IN SITU REMEDIATION PROCESS

The remediation process used at the OBP was in situ chemical oxidation using a 50% concentration of hydrogen peroxide to treat organic contaminants found at the site. This process offers a cost-effective alternative with short-term (i.e., months versus years for other in situ techniques) results. Chemical oxidation of organic contamination can be achieved by the injection of a hydrogen peroxide and catalyst formulation into the affected media under properly controlled conditions using injectors similar in design to groundwater monitor wells. This in situ oxidation is capable of complete, nonselective oxidation of organic compounds in soil. The oxidative process is simplified below:



During the reaction sequence, the organic compounds are successively converted to shorter chain mono- and di-carboxylic (fatty) acids. These compounds are similar to the naturally occurring fatty acids that are nonhazardous. The fatty acids are further degraded by this process to carbon dioxide and water. Chlorinated VOCs are broken down in the same reaction sequence. Chlorine ions are degraded from the halogenated compounds before the fatty acid degradation sequence of the reaction. The actual oxidation is driven by formation of the hydroxyl free radical via Fenton's Reaction Chemistry. This methodology for the treatment of organic compounds and toxins in wastewater has been widely studied, used, and proven effective by the wastewater industry since the early 1900s. The preferred Fenton's Reaction is:

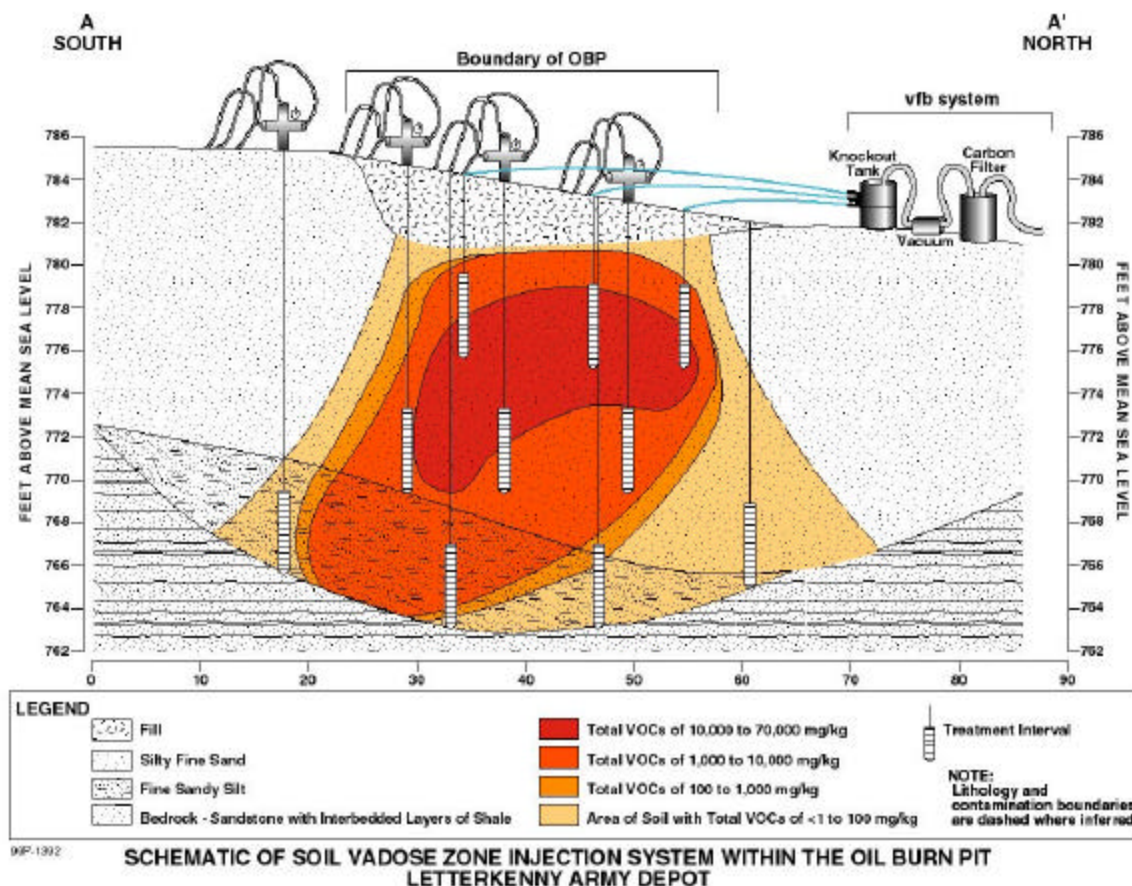


The hydroxyl free radical (OH^+) is an extremely powerful oxidizer capable of oxidizing complex organic compounds. Residual hydrogen peroxide, due to its unstable characteristics, rapidly decomposes to water and oxygen in the subsurface environment. Soluble iron amendments are added with the catalyst solution in trace quantities during the injection process and are precipitated out during conversion to ferric iron.

1.4 SYSTEM DESIGN

The injection system design includes injectors installed at multiple depths, a delivery system for the chemical oxidation and catalyst solutions, and a vacuum system. **Figure 1** shows a schematic of the soil vadose zone injection system.

Figure 1



The injection system components shown in **Figure 1** are summarized below:

- **Injectors** - 21 injectors were installed across deep (17 to 23 ft bgs), intermediate (12 to 17 ft bgs), and shallow (7 to 12 ft bgs) depth intervals to provide the vertical and horizontal spacing needed to chemically oxidize the organics present in the vadose zone soils. Both single and dual (i.e., shallow and deep) injectors were installed with a horizontal spacing of 5 to 10 feet. The single injectors were installed in 4-inch outer diameter (OD) boreholes while the dual injectors were installed in 8-inch OD boreholes. The injectors were constructed with 1 to 5 ft long stainless steel screens (gauze size #40-0.017 inch) attached to 1.25 inch or 2 inch diameter Schedule 40 black steel riser pipes. The open borehole space around each injector screen was packed with Morie No. 1 sand to approximately 1ft. above the top of the screened interval. A 6-inch to 1-ft bentonite seal was placed on top of the sand interval. A cement/bentonite grout was tremmied from the top of the bentonite seal to the surface. Each injector had a stickup of approximately 6-inches to 1.5 ft that was threaded at the top to permit the attachment of an injector head.

- **Injector Head** - The injector head consists of three delivery ports with valves and a pressure gauge equipped with a high-pressure blowout valve. The head is constructed with steel components designed to withstand high backpressures that may occur during injection. High-pressure hoses are attached to each port for delivery of hydrogen peroxide, catalyst, and air. The hoses run from each injector head to the support trailer, which contains the hydrogen peroxide and catalyst solutions. Up to four injector heads were operated simultaneously.
- **Vacuum System** - A vacuum system or vapor flow balance system (vfb system) was attached to a portion of the unused injectors. The vfb system was used to help relieve subsurface pressures generated during the reaction, remove VOCs released during the heating of the soils, and to help cool the soil after the injection process was complete to shorten the waiting period needed to obtain post-injection confirmation samples. The discharge from the vfb system was directed through a knockout tank (to remove moisture) then through a charcoal filter.

During injection, chemical oxidation fluids are added to a target soil interval using three injectors, while a fourth injector is used to create an oxidative barrier in a deeper zone to treat any VOCs that may be mobilized downward. Gases and fluids generated during the chemical reaction are released at the surface in the form of off gas, liquid, and steam. The rate of these releases is monitored and is adjusted to ensure that they do not develop into pathways for hydrogen peroxide to short-circuit and reach the surface. The progress of the chemical oxidation reaction is documented by monitoring increases in soil temperatures and by using a field instrument to monitor injectors directly above or adjacent to an injection zone for the presence of oxygen (O₂) and carbon dioxide (CO₂). The presence of carbon dioxide concentrations above 1% indicates that organic compounds are still being oxidized. As CO₂ levels drop below 1% and O₂ concentrations increase, the injection is shifted to another target zone. The addition of chemical oxidation fluids continues until CO₂ concentrations drop below 1% and high O₂ concentrations are observed throughout the treatment area.

1.5 OPERATION SUMMARY

The soil vadose zone injection was conducted in two phases. Phase 1 was conducted for approximately 2 weeks between June and July 1997 while Phase 2 was conducted for approximately 5 weeks between October and November 1998. Approximately 24,000 gallons of a 50% hydrogen peroxide solution were injected over these two phases. The Phase 1 injection was discontinued because the hydrogen peroxide injected into the shallow zone was prematurely short-circuiting to the ground surface. The short-circuiting occurred because the high levels of VOCs in the shallow soil zone generated strong offgas pressures when oxidized by the hydroxyl free radicals. These strong offgas pressures created preferential pathways through the unconsolidated fill material that had been used to backfill the OBP. Prior to conducting the Phase 2 injection, bench scale tests were conducted to further evaluate the chemical oxidation process, five new injectors were installed to provide additional injection coverage and/or to act as vents for the shallow soil zone, and a soil/cement cap was installed in the top 18 inches of the fill material to seal the preferential pathways created during Phase 1 injection.

The highest soil temperature recorded during injection was greater than 158 degrees Fahrenheit (°F) (the maximum reading of the thermometer). Post-injection temperatures ranged above ambient temperatures (approximately 60° F) for approximately 3 months after each phase of the

injection. Carbon dioxide concentrations were recorded during injection at an average concentration of 10% with some spikes to 20%, while oxygen levels ranged from 25% to over range (>30%).

Thirty-one post-injection soil confirmation samples were collected for the Phase 1 injection and 30 post-injection soil confirmation samples were collected for the Phase 2 injection. Both sets of samples were collected from 10 soil boring locations and were analyzed by a fixed-based laboratory for VOCs using EPA SW846 Method 8260B. Samples were collected for analyses from soil zones with the highest readings recorded by the organic vapor monitor (OVM) field instrument.

1.6 RESULTS/CONCLUSIONS

The results of the Phase 1 post-injection soil confirmation samples indicated that high concentrations of VOCs were still present in the shallow soil zone. The bench scale tests conducted between the Phase 1 and 2 injections indicated the following:

- An effective reduction in soil VOC concentrations could be achieved.
- A ramped approach, where hydrogen peroxide is introduced to the soil at slowly increasing concentrations is warranted to ensure the reaction is not too aggressive.
- Aggressive utilization of the vfb system would help maximize the remove of VOCs in the offgas.

Phase 2 post-injection soil confirmation samples indicated that a substantial reduction had been achieved in the mass of VOCs present in the OBP soils. The maximum concentrations of 1,1,1-TCA and total VOCs detected in the Phase 2 post-injection samples were 4,900 mg/kg (maximum pre-injection 49,000 mg/kg) and 10,093 mg/kg (maximum pre-injection 70,000 mg/kg), respectively. A sample collected adjacent to the location with the highest pre-injection concentration of 1,1,1-TCA (49,000 mg/kg), had a 1,1,1-TCA concentration of 68 mg/kg. A 3-dimensional geospatial computer model (earthVision®) was used to calculate pre- and post-injection total VOC and 1,1,1-TCA mass in OBP soil based on site-specific assumptions. The geological and soil chemical data collected at the OBP before and after injection was inputted into the model. A comparison of the total VOC and 1,1,1-TCA pre-injection mass and Phase 2 post-injection mass are provided in **Tables 1 and 2**, respectively.

Table 1
Estimated Total VOC Contaminant Mass Present
in Pre-Injection and Phase 2 Post-Injection OBP Soils

VOC Comparison Concentration	Pre-Injection Mass of VOCs	Post-Injection Mass of VOCs	Estimated Mass Reduction
Total VOCs >7 mg/kg	5,037 lbs	1,183 lbs	77%
Total VOCs >500 mg/kg	4,968 lbs	1,009 lbs	80%
Total VOCs >3,000 mg/kg	3,966 lbs	310 lbs	92%
Total VOCs >5,000 mg/kg	3,149 lbs	33 lbs	99%

mg/kg = milligrams per kilogram.

lbs = pounds

Table 2
Estimated 1,1,1-TCA Contaminant Mass Present
in Pre-Injection and Phase 2 Post-Injection OBP Soils

VOC Comparison Concentration	Pre-Injection Mass of VOCs	Post-Injection Mass of VOCs	Estimated Mass Reduction
1,1,1-TCA >7 mg/kg	3,060 lbs	526 lbs	83%
1,1,1-TCA >500 mg/kg	2,971 lbs	378 lbs	87%
1,1,1-TCA >2,000 mg/kg	2,317 lbs	60 lbs	97%
1,1,1-TCA >4,000 mg/kg	1,578 lbs	1 lb	99.90%

mg/kg = milligrams per kilogram.

lbs = pounds

The overall estimated mass reduction of total VOCs and 1,1,1-TCA from the soil vadose zone injection is approximately 77% and 83%, respectively. Because VOC concentrations remain above the generic Act 2 standards established as cleanup goals for the site, a baseline risk assessment is being conducted as part of the ongoing Remedial Investigation (RI) to see if remaining contaminants pose an unacceptable risk based on future land use.

1.7 REFERENCES

Commonwealth of Pennsylvania. November 1996. *Pennsylvania's Land Recycling Program – Technical Guidance Manual*. Pennsylvania Department of Environmental Protection

WESTON (Roy F. Weston, Inc.). 1997. *Technical Plan for CERCLA Removal Action: In Situ Remediation of Vadose Zone Soils and a Pilot Study for In Situ Remediation fo the Bedrock Aquifer at the PDO OU4 Oil Burn Pit, Final*. Prepared for the U.S. Army Environmental Center, Installation Restoration Division, Aberdeen Proving Ground, Maryland.