

Remediation of Soils Contaminated With Tetrachloroethene

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In recent years, significant advancements have been made in the remediation of soil contaminated with volatile organic compounds (VOCs), including tetrachloroethene (perc). Until recently, the options available were cumbersome, time-consuming, expensive and in some cases quite dangerous. Typically, they included excavation with either off-site disposal or on-site thermal treatment. By regulation, the excavated soils were classified as a hazardous waste. This significantly increased the costs of disposal or treatment. Moreover, if contaminated soils are disposed at a landfill, future liabilities remain with the generator.

In-situ soil vapor extraction (SVE), a common alternative to excavation, avoided the hazardous waste issue; however, soil conditions such as clay often preclude the applicability of SVE systems. Where these systems are used, remediation takes years to complete and actual site closures are rare. The installation price, annual operating expenses, extended monitoring programs and the ever increasing cost of energy accrue to make remedial systems a costly endeavor.

The client that is the subject of this paper, was faced with severely limited alternatives at an industrial facility, impacted with perc. This site presented several difficulties. Low permeability soils rendered SVE technically infeasible. Although excavation was an option, utilities and heavy vehicle traffic significantly restricted the accessibility. Additional concerns arose because the impacted soils were adjacent to the foundations of a 100-year-old masonry building. Consequently, excavation would have resulted in complicated shoring and much of the contaminated soil being left in-place. Because perc concentrations as high as $6,440,000~\mu g/Kg$ were detected in these soils, this alternative was considered unacceptable.

Fortunately, an alternative technology was available. Contaminants, whether gasoline, perc, or other VOCs, are chemicals. When given the chance to react with appropriate other chemicals, they can be reduced to harmless by-products. Such a process, researched and developed William Lundy, was implemented at the site.

Process Description

The technology selected, first chemically oxidizes contaminants to form oxygenated organics (alcohols or similar compounds) which are subsequently biologically mineralized by indigenous microbes. The process exploits the very powerful oxidizing agents, generated insitu from peroxygen compounds. Although hydrogen peroxide was first commercially used in the 1970s by Lundy, at the time a researcher with Shell Chemical Company, to oxidize hydrogen sulfide in potable water and sewage, its use as an in-situ remediation tool did not emerge until well into the 1990s. Instead, bioremediation became the more popular of choice. Unfortunately, many compounds, especially those containing chlorine (e.g., perc), proved resistant to most bacteria. Chlorinated compounds' low rate of biodegradation is due, in part, to their toxicity to microorganisms. However, while resistant to biodegradation, most



chlorinated compounds (including perc) are quite vulnerable to chemical oxidation; a reaction that is well understood and widely used by industry in the commercial production of alcohols.

Although liquid hydrogen peroxide can be readily applied to soils and groundwater, several negative factors have raised concerns both with regulators and engineers. The low pH (3), necessary for optimum oxidation (Fenton reaction), attacks soils, particularly where high concentrations of carbonates (e.g., limestone) are present. Also, to facilitate oxidation, a mixture of hydrogen peroxide and iron salts are usually co-injected. The reaction of these two compounds is highly exothermic and produces extreme heat. In fact, it is not unusual to see temperatures well above the boiling point of water. In this case, contaminant volatilization becomes a potential problem and the injection method itself may further exacerbate existing site problems.

The conventional method of application for the Fenton reaction is through steel injection wells. To assure that the peroxide contacts the contaminants, a large volume of liquid must be injected in each well. This technique, coupled with the extreme rise in temperature and the production of gas, greatly increases the probability of pushing the contaminant plume. Moreover, remediation is generally limited to treating only porous strata such as sand or gravel. The oxidation process selected has solved these field application problems.

The major draw-back of in-situ remediation processes had been the lack of ability to place reagents in contact with the contaminants. This limitation has been significantly overcome because the process is able to evenly permeate the contaminant plume without the need for injection wells. Using a liquid drilling technique similar to that used in oil field exploration, the process creates a high velocity fluid jet which liquefies the soil at the injector tip. This allows the probe to be easily advanced by hand. Because liquid accomplishes the drilling, the safety and protection of subsurface structures and utilities are assured and since injection wells are not needed, there is no limit to the number or location of injection points.

By placing a smaller volume of reagent in a larger number of points, the required volume of reagent specified for treatment can be injected evenly over the site. This minimizes the chance of areal expansion of the contaminant plume while greatly reducing the problem of treating heavy more impermeable soils such as clays or silts. Because the injector is hand-held, contaminants under buildings are easily reached by drilling small access holes through slabs or basement floors, and, if needed, angular injection can also be used from outside the structure.

Like the Fenton reaction, destruction of contaminants occurs by the addition of hydroxyl groups (hydroxylation) to the carbon molecule. The resulting daughter compounds (alcohols, etc.), are readily metabolized by a much wider variety of microbes than those specific to the original contaminants. And, because the reaction is controlled, it eliminates the heat and pressures prevalent with systems that use only liquid hydrogen peroxide.

When the initial oxidation stage is completed, the reagent system continues to produce molecular oxygen and nutrients to enhance biodegradation. However, unlike passive



biodegradation, the oxidation process can readily destroy high concentrations of contaminants within days or even hours.

Results

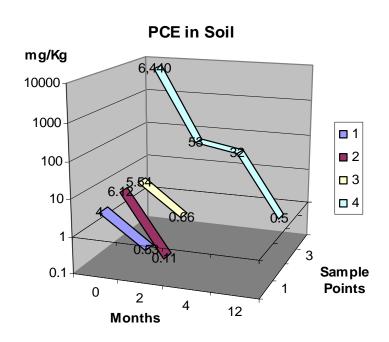
Two months after the first reagent application, soil samples were collected and analyzed from the four most heavily contaminated areas. Perc concentrations (or those of its breakdown compounds) from before the application and two months later, are summarized in Table I below.

Table I PCE Concentrations (mg/kg) Soil

Locatio	n Original	2 Months	4 Months	12 Months
GP-1	4.00	0.53^{1}		
GP-2	6.12	0.11^{1}		
GP-3	5.54	0.66^{1}		
GP-4	6,440	53	32^{2}	$0.52^{1,3}$
1 N	Meets cleanup criterion of 1 mg/kg.			

² Second application.

Under most circumstances, post treatment concentrations would not be high enough to require multiple applications; however, at the location of GP-4, the concentrations required a second and third application. both subsequent After applications, the concentrations at that location continued to decline. Subsequent to the second application the source area was pin-pointed under the foundation of the building near GP-4. During the third application, this area was directly accessed using angular injection techniques. Sampling results completed after the third



application to the GP-4 area, revealed that the cleanup goal of 1 mg/kg had been attained. The site has been submitted to the agency for no further action.

³ Third application.



Costs

As with all aspects of site investigation and remediation, it is not possible to assign specific costs to the remedial methods discussed above. However, a comparative study of total project costs would indicate that the price of the in-situ chemox application varied from forty percent (40%) to eighty percent (80%) less than the cost of excavation and disposal. This same cost savings range appears to hold true for SVE systems and is even more competitive when the cost of operation and maintenance of those systems is included. Note that the costs for disposal are based upon an assumption that the soil would qualify as non-hazardous; however, perc often results in a hazardous classification, which would more than triple the disposal costs. It is also interesting to note, that the over-all cost of chemox treatment is a fraction of the cost of incineration. This is an extremely important factor where herbicides or pesticides are the target of the remedial project.

Summary

In the discussion presented herein, we have described the application of a revolutionary approach to the remediation of soils contaminated with perc and other VOCs. This method, when combined with risk-based, site-specific cleanup goals, can significantly reduce the costs of attaining site closure. However, significant additional benefits are inherent in the process. Some of these include:

- *Elimination or future Liabilities*: This process results in the destruction of contaminants in-situ and on-site, thus eliminating the potential for future environmental liability from off-site disposal.
- **Discrete Process**: Rather than presenting the neighborhood with a display of heavy equipment, the technology is installed with little more fanfare than that associated with most lawn care services.
- Minimal Site Disturbance: During the application, only relatively small areas are occupied by the installation equipment. Thus, in the case of service station or most other site work, the owners business is not interrupted and only minimal disturbance is expected. When the site work is completed, there are little or no signs of the activities that have occurred.
- **No Operation & Maintenance Cost**: The reagent is applied, followed by the collection and analyses of a few confirmatory samples. There is no system to operate, maintain and monitor.

For more information on this approach, or if you would like to evaluate its applicability at your site, call Bob Nauta (RSV Engineering, Inc. - 920-674-3411 email bnauta@rsv-engineering.com) or Bill Lundy (708-396-0100) – email w.lundy@comcast.net

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