



Project Summary

Field Studies of *In Situ* Soil Washing

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The EPA and U.S. Air Force conducted a research test program to demonstrate the removal of hydrocarbons and chlorinated hydrocarbons from a sandy soil by *in situ* soil washing using surfactants.

Contaminated soil from the fire training area of Volk Air National Guard Base, Wisconsin, was first taken to a laboratory for characterization. At the laboratory the soil was recompactd into glass columns creating a simulated *in situ* environment. Under gravity flow, 12 pore volumes of aqueous surfactant solutions were passed through each of the columns. Gas chromatograph (GC) analyses were used on the washing effluent and soil to determine removal efficiency (RE). The results of these tests were highly encouraging. RE's of field tests run at the fire training area were evaluated by GC, total organic carbon (TOC) and oil and grease data. Ten one foot deep holes were dug in the surface of the fire pit. Surfactant solutions were applied to each hole at a rate of 1.9 gallons per square foot per day. Soil samples, taken from the undisturbed layers beneath each hole, were analyzed for residual contamination. Samples experiencing a flow through of nine to fourteen pore volumes of surfactant solution still had contaminant levels comparable to 5,000-10,000 $\mu\text{g/g}$ prewash conditions.

The field study also included the development of a groundwater treatment process. Measurements of TOC, VOA and biochemical oxygen demand (BOD₅) were decreased by 50%, 99%, and 50%, respectively.

Treated effluent was discharged directly to the on-base aerobic treatment lagoons.

This Project Summary was developed by EPA's Hazardous Waste Engineering Research Laboratory, Cincinnati, OH, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).

Introduction

Surface and near-surface contamination often serve as the source for groundwater contamination. Percolation of rainwater through spill sites quickly carries soluble and semi-soluble contaminants away from the point of origin. Contaminants considered "insoluble" above parts per million nevertheless migrate more slowly. Gross contaminant sources supply pure product that over many years, flows deeply through unsaturated soils.

Part of the EPA's Superfund site cleanup research has been directed at washing such contaminated soil with the aid of aqueous surfactant solutions. The research takes two directions. The first is to excavate the soil and mix it in a wash solution. The second research objective concentrates on the application or injection of a surfactant solution into undisturbed soil *in situ*. A segment of this *in situ* research is the subject of this project summary.

This demonstration effort grew out of mutual need between the EPA and the U.S. Air Force. From 1982 to 1985 the EPA researched soil washing technology using surfactants in laboratory studies. Recompactd soils were used in these studies to simulate *in situ* conditions

Truly undisturbed contaminated soil was not tested up to that time. The U.S. Air Force, as part of its Installation Restoration Program, was seeking processes to clean up 128 fire training pits at Air Force installations. The Air Force selected the Air National Guard Base in Camp Douglas, Wisconsin, as a candidate site for the EPA to test either excavated or *in situ* soil washing. The EPA and the Air Force representatives chose *in situ* washing after further consideration.

The Laboratory Study

Previous laboratory work identified a 50/50 blend of two commercially available surfactants that work well in removing contaminants from soil. They are Adsee 799 and Hyonic PE-90, sold by Witco Chemical and Diamond Shamrock, respectively. To determine if this same blend would work at the Volk Field fire training pit, contaminated soil samples were collected.

Five physical tests characterized the soil. They were: grain size, TOC, cation exchange capacity (CEC), mineralogy by x-ray diffraction, and permeability. The grain size of the contaminated soil was 98% sand. By x-ray diffraction, alpha-quartz comprises the major portion of the soil with a minor amount of feldspar being present. TOC was as high as 14,900 µg/g. The cation exchange capacity of 5 milliequivalents/100 g was not significant to the contamination levels, however, it did support the x-ray diffraction mineralogic findings. The permeability of the fire pit soil, at 10^{-3} and 10^{-4} cm/sec, was one to two orders of magnitude less than adjacent uncontaminated soil.

Chlorinated hydrocarbons were part of the volatile contamination. Dichloromethane, chloroform, 1,1,1-trichloroethane (TCA), and trichloroethylene (TCE) at concentrations up to 3 ppm and total chlorinated solvents up to 3.5 ppm were determined by the VOA procedure. Other hydrocarbons are aliphatic, aromatic and polar constituents. The level of hydrocarbon contamination is in the hundreds of µg/g based on the laboratory analysis.

Contaminated groundwater, a significant problem, from the aquifer below the fire training pit, was also characterized in the lab study. VOA, TOC, and ultraviolet spectroscopy (UV) was used. The investigations determined that the groundwater contains chlorinated and non-chlorinated hydrocarbons in excess of 300 ppm.

The soil adsorption constant (K) is a measure of a pollutant's tendency to adsorb and stay on soil. A value of 2,000 for PCB's indicates a two-hundred-fold greater adsorption (holding power) than benzene at $K=10$. Benzo(a)pyrene, a toxic substance, and oil have similar values - $K = 30,000 - 40,000$. Grouping contaminants according to a K value and evaluating removal efficiencies (RE) gives order to an otherwise complex collection of chemical classes. This is a report of the EPA's and the U.S. Air Force's field evaluation of *in situ* soil washing of compounds having K values between 10^1 and 10^6 .

The Field Study

The field study was conducted by laying out ten 2' x 2' x 1' pits, dug into the contaminated surface of the fire training area, which served as reservoirs that held various surfactant solutions. Field technicians applied wash solutions into the holes at the maximum rate of 1.9 gallons per square foot per day. The daily dosage was applied in four increments. Since each hole percolated the solutions at different rates, the time interval between doses varied from hole to hole. Testing in three of the pits stopped when the time intervals for the next application approached ten hours indicating unacceptable permeabilities being created. Following seven days of washing, the pits received rinses with local, potable well water.

A combination of infrared spectroscopy (IR) and gravimetric determinations of soil extracts was used to evaluate "before and after" contaminant concentrations. To determine contaminant concentration, soil samples were taken after the rinse process, extracted with carbon tetrachloride, and analyzed by IR spectrophotometer for spectral absorbance by the carbon hydrogen bond. The extracts were then air dried and weighed to determine gravimetrically the contaminant concentration (non-volatile).

The contaminant concentration before soil washing was based on the extracts of soil samples taken adjacent to the test holes. No samples were taken directly from the test holes before washing in order not to bias permeation rates.

Based on both the gravimetric and IR determinations of contaminant concentrations, there was no measurable decrease in contaminants following as many as 14 pore volumes of soil washing in the field tests.

In addition to the soil washing, field crew conducted a bench-scale groundwater treatment study. From study a treatment system was assembled and operated which successfully reduced TOC, VOA and BOD₅ by 50, 99, 50%, respectively. At these effluent levels, discharge to the local aerated sewage lagoon was below the Wisconsin Department of Natural Resources' permit limits. A total of 320,000 L of contaminated groundwater was treated at rates of 15,000 to 45,000 L/day.

The bench-scale study investigated the use of lime, alum, ferric sulfate, hydrogen peroxide, polymeric electrolytes and mineral acids. The application of these chemicals was guided by conventions appropriate to wastewater treatment plants. The resulting wastewater treatment process (shown in Figure 1) was based on the addition of lime at 1 g/L. The lime created a flocculation of iron oxides and organics. The contaminant plume contained up to 100 mg/L iron. Particulate sedimentation, clarifier, followed by additional residence time in a holding lagoon, reduced TOC, BOD₅, and VOA to acceptable discharge levels. A final polishing of volatiles in an air stripper was the last step in the process. Table 1 is a summary of the analytical data.

Conclusions

1. *In situ* soil washing of the Volk Field fire training pit with aqueous surfactant solutions was measurably effective. It is likely that this same ineffectiveness would occur at other chronic spill sites that have contaminants with high soil-sorption values ($K > 10^3$).
2. *In situ* soil washing requires groundwater treatment. Groundwater treatment at this site was very successful with the simple addition of lime. Air stripping effectively removed the volatile organics. Advantages of this site were its remoteness, workable air emission limits that facilitated groundwater treatment operations and a local sewerage treatment system owned by the responsible party. TOC levels of recovered groundwater were reduced to one half the initial values by precipitation with lime which allowed for direct discharge to the aerated treatment lagoons. Obviously, not all waste sites have these favorable conditions. Other fire pit sites with lower effluent limits would require systems with greater retention times.

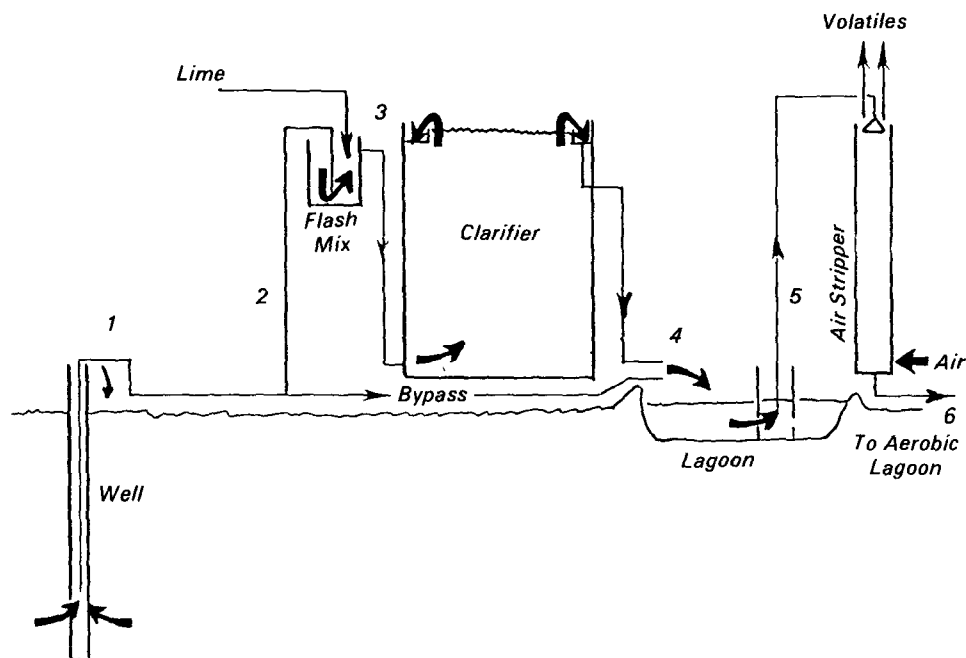


Figure 1. Volk Field pilot treatment for water.

Table 1 Analytical Tests and Sampling Points for the Water Treatment Process

Pt No.	Description	Tests Performed	Approximate Values, Average or Range
1	Individual well head	volatile organic total organic chemical oxygen demand oil and grease pH	10-20 mg/liter 60-760 mg/liter 6-500 mg/liter 0.2-46 mg/liter 5.1-6.2
2	Well field effluent	volatile organic total organic iron pH chemical oxygen demand flow rate	10-20 mg/liter 250 \pm 14% mg/liter 32 mg/liter 6.0 \pm 0.2 41 mg/liter .25 - 2 liter/sec
3	Flash mixer effluent	total organic (dissolved) suspended solids pH flow rate	160 mg/liter 350 mg/liter 6.8-9.7 .5 - 2 liter/sec
4	Clarifier effluent	total organic suspended solids pH flow rate	205 \pm 7% mg/liter 13.6-104 mg/liter 7.6 .5 - 2 liter/sec
5	Air stripper feed	volatile organic total organic temperature flow rate (water) oil and grease	3.5 - 7.0 mg/liter 151 \pm 13% mg/liter 6-15°C 95 - 126 liter/sec 3.6 mg/liter
6	Air stripper effluent	volatile organic total organic flow rate (air) oil and grease biochemical oxygen demand chemical oxygen demand	0.3 - 0.5 μ g/liter 146 mg/liter 101 l/sec 3.6 mg/liter 2.5 mg/liter 180 mg/liter
7	Clarifier	suspended solids	4.4 mg/liter
8	Clarifier bottom	suspended solids	2331 mg/liter
9	Soil	oil and grease	800-16000 mg/kg

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U.S. GPO 548-013