

OPTIMIZATION OF THE SOIL MIXING/THERMALLY ENHANCED SOIL VAPOR EXTRACTION PROCESS BY ZERO-VALENT IRON ADDITION

L. Moos, R. Swale, and P. Lynch
Argonne National Laboratory-East, Argonne, IL
and
R. Murray, P. LaMori, and C. Siatro
In-Situ Fixation, Inc., Chandler, AZ

ABSTRACT

The 317 Area of Argonne National Laboratory-East contains soil contaminated with a series of chlorinated volatile organic compounds (VOCs) as a result of past waste disposal practices. Because of the low permeability of the native clay soil in the region, an innovative soil treatment process was chosen. This process, known as soil mixing with thermally enhanced soil vapor extraction (SM/TESVE), was selected because of its ability to remove a wide variety of VOCs from low-permeability soils. However, this technology alone was not able to achieve the remediation objectives for this site. To achieve the necessary additional removal, three soil treatment technologies were evaluated to determine their suitability as polishing treatments. The polishing techniques evaluated included soil ventilation, augmented indigenous biodegradation, and metallic (zero-valent) iron addition. Each polishing system was deployed following SM/TESVE treatment of the experimental area. The field trials indicated that the addition of metallic iron was by far the most effective treatment technique of the three tested. The zero-valent iron polishing technique was utilized during the full-scale remedial action. This treatment approach resulted in improved treatment effectiveness; the residual VOC concentrations were reduced by more than a factor of 10, as compared with the SM/TESVE process alone. Removal efficiencies greater than 99% were observed when both the SM/TESVE and iron treatment were used, as compared with 70 to 80% for SM/TESVE alone. Because iron addition allowed the SM/TESVE process equipment to be used more efficiently, greater removal efficiency was achieved with minimal increase in cost.

INTRODUCTION

The 317 Area of Argonne National Laboratory-East (ANL-E) is an active radioactive waste processing and storage area. During the 1950s, this area was also used for the disposal of various liquid chemical wastes into a unit known as the 317 Area French drain. As a consequence of this past practice, several chlorinated and nonchlorinated volatile organic compounds (VOCs) have been detected in the soil and groundwater beneath the 317 Area.

In late 1997, ANL-E began the process of removing the organic contaminants from the soil near the French drain. Because the soil at the ANL-E site consists of highly impermeable clay, common techniques for removing the contaminants, such as soil vapor extraction, would not have been effective. After evaluating numerous technologies, ANL-E selected a process known as soil mixing with thermally enhanced soil vapor extraction (SM/TESVE) (1,2).

The SM/TESVE process utilizes a soil mixing apparatus, a hydraulically powered auger assembly, to break up and mix a column of soil up to 9 m (30 ft) deep. At the same time the soil mixing is occurring, a mixture of steam and hot air is pumped down the hollow stem of the auger assembly where it exits at the tip of the auger stem. The steam and hot air cause the VOCs in the soil to diffuse into the air stream, where they are carried to the surface. The off-gas is then captured in a shroud and treated in an off-gas treatment system (3). Fig. I is a photograph of the soil mixing rig used in this project. The augers are under the white shroud shown in this photograph.



Figure I Soil Mixing Rig

Treatability studies of this technology indicated that the SM/TESVE process could economically remove approximately 70 to 80% of the VOCs present. However, the initial contaminant concentrations were high enough that over 95% removal of VOCs was necessary to meet cleanup objectives. To meet these objectives, it would be necessary to perform a polishing soil treatment operation following SM/TESVE. Bench-scale treatability studies of six polishing treatment systems were performed, including soil vapor extraction, metallic iron addition, augmented indigenous biodegradation, chemical oxidation (using potassium permanganate), a proprietary humic acid-based treatment compound known as Humasorb (manufactured by ARTECH Inc., Sterling, VA), and Daramend, a proprietary treatment compound (manufactured by Grace Dearborn, Mississauga, Ontario) (1).

After an analysis of the results of the treatability studies, the three most promising treatment technologies were chosen for further evaluation under field conditions. This evaluation was a side-by-side comparison of soil vapor extraction (referred to as soil ventilation in this report to avoid confusion with the SM/TESVE process), enhanced biodegradation using endogenous bacteria, and metallic iron addition. The results of this investigation were used to select the polishing treatment system used for the full-scale treatment.

PROJECT BACKGROUND

Site Background Information

The 317 Area contains several active waste-processing facilities, including a series of in-ground concrete storage vaults, a mixed waste storage pad, and other facilities. A former waste disposal facility, known as a French drain, is also present. This facility consisted of a shallow gravel-filled trench. Liquid wastes were poured onto the gravel in the trench, where they soaked into the underlying soil. The French drain was actively used from the mid to late 1950s. Fig. II is a sketch of the 317 Area showing the location of the former French drain.

Site Geology

The soil underlying the 317 Area consists of a mixture of glacially deposited clays, sand, and gravel and is approximately 21 m (70 ft) thick. This soil overlies weathered dolomite bedrock. The glacial till material consists primarily of dense clay with interbedded layers of silt, sand, and gravel. The silt, sand, and gravel layers are thought to be typically discontinuous, but could be interconnected to varying degrees. The clay layers were measured to have a hydraulic conductivity of approximately 1×10^{-8} cm/s. This very low permeability greatly impedes the vertical movement of water through the soil (4).

Description of Contamination

A Resource Conservation and Recovery Act (RCRA) facility investigation of this area was completed in 1997. This investigation revealed a region of highly contaminated soil near the French drain that extended to a depth of approximately 9 m (30 ft). Contaminants detected in this area were almost exclusively VOCs. Table I shows the principal contaminants detected and the maximum concentrations in the soil prior to the start of the project.

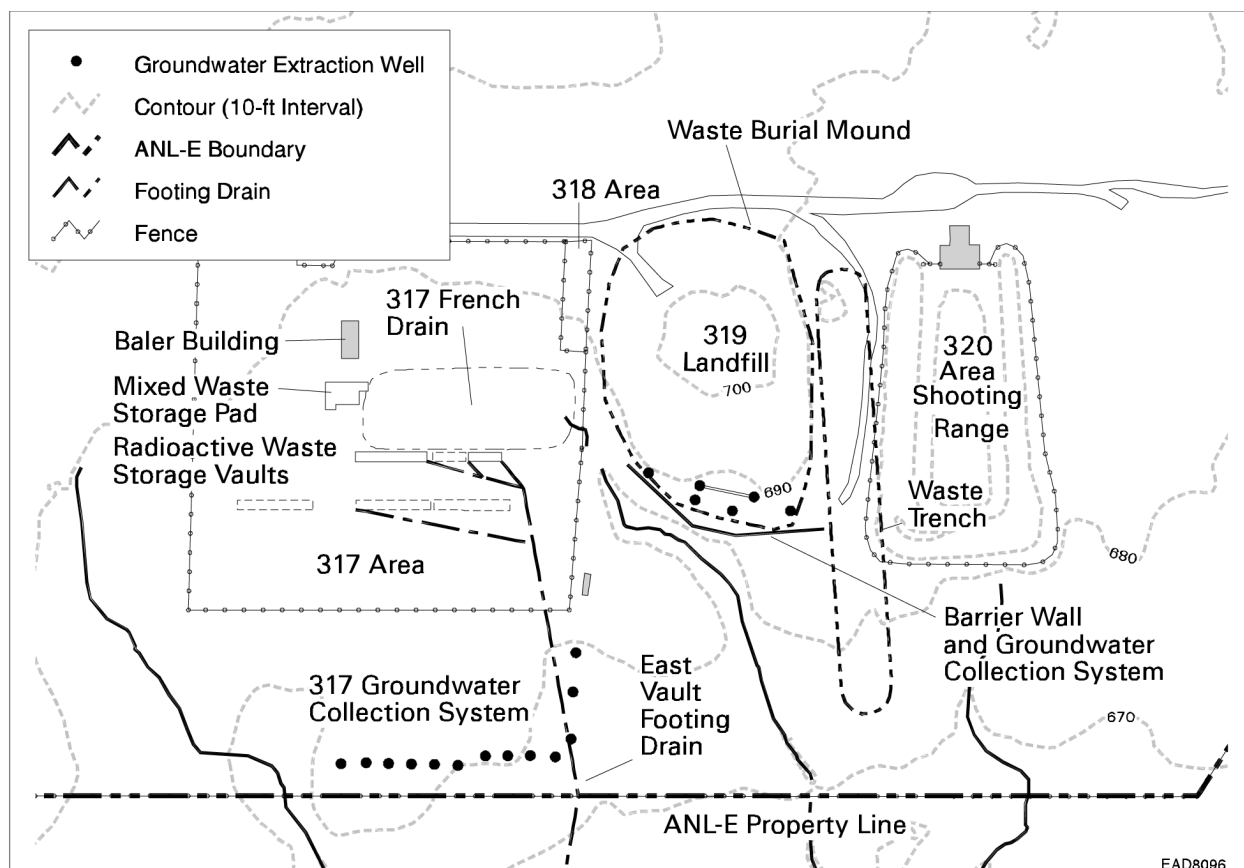


Fig. II 317 Area and Surrounding Area

Table I Highest Concentrations of Principal Contaminants Detected in Experimental Area (2)

Constituent	Concentration (µg/kg)
Acetone	3,300
Benzene	19,000
Carbon tetrachloride	180,000
Chloroform	51,000
1,2-Dichloroethene (total)	3,200
Isobutyl alcohol	39,000
4-Methyl 2-pentanone	8,000
Methylene chloride	3,000
Tetrachloroethene	71,000
Toluene	4,400
Trichloroethene	180,000
Xylene (total)	37,000

Because of the nature of the disposal method used and the highly heterogeneous nature of the soil, the distribution of contaminants was also highly heterogeneous. Contaminant concentrations were found to vary by orders of magnitude within a few inches of vertical or horizontal distance. The mixture of contaminants at a given location also varied greatly.

PROJECT DESCRIPTION

The soil treatment method used for the full-scale remediation project, SM/TESVE, was selected because of its capability to remove a wide variety of volatile contaminants from highly impermeable clay soil without the need to excavate and treat the soil above ground. Fig. III is a process schematic of this system.

Experiment Deployments

The experiment deployments, as well as the subsequent full-scale treatment of the 317 Area French drain soils, were performed by In-Situ Fixation, Inc. (ISF) of Chandler, Arizona. ISF used a mobile dual-auger soil mixing system equipped with special soil mixing blades it designed for clay soil. Steam injection heated the soil and air stream. Off-gas was collected under a steel shroud that completely surrounded the augers. An off-gas activated carbon treatment system was attached to the shroud to ensure that all off-gas was captured and treated before being discharged to the atmosphere. Fig. I shows the rig and shroud.

The three initial polishing treatments plus one control area were deployed within the contaminated region. Four additional follow-on iron injection studies were also performed. The test areas were labeled sequentially from XA1A to XA10 (experiment XA5 was planned but never implemented).

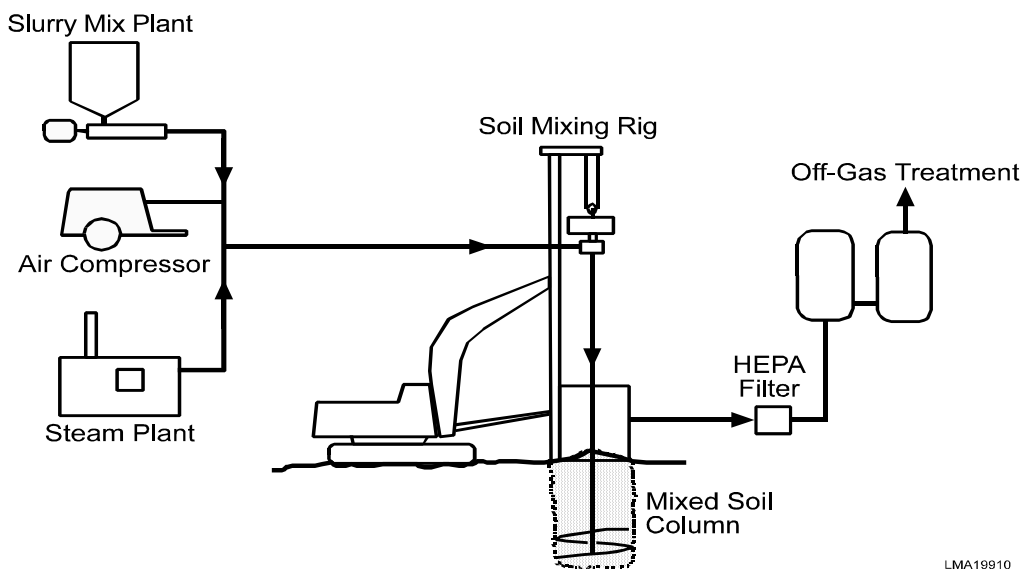


Fig. III Soil Mixing Process Schematic

All three polishing processes were selected such that they could be integrated with the SM/TESVE process. The selected technology would be deployed during or following the SM/TESVE operation. The normal SM/TESVE process was first performed in each of the four areas. This soil mixing operation loosened and homogenized the soil; the steam added heat and moisture. This step removed approximately 70 to 95% of the chemicals originally present.

The soil ventilation system (XA1A) was constructed by installing two polyvinyl chloride well screens in the mixed soil column with a hollow-stem auger rig. A vapor extraction system was attached to one of the wells. The other well then served as an air inlet pipe. The air extraction system was fitted with flow and pressure monitoring devices, a high-efficiency particulate air filter, and a modular activated-carbon absorber unit.

The augmented indigenous biodegradation test (XA4) was deployed by using the soil mixing apparatus to inject and mix a solution containing a nutrient mixture and methanol. The nutrient solution was a combination of a commercial growth-enhancing product (Humega, BioFlora International, Goodyear, AZ) and ammonium polyphosphate. Laboratory-grade methanol was also added. The nutrients and methanol were mixed with water that was then pumped into the soil through the hollow auger stem (Kelly bars).

The initial iron-addition experiment (XA3) was deployed by using the soil mixing apparatus to inject and mix a slurry of iron powder and guar gum (50% iron, 50% water with a small amount of guar gum powder added) into the test area. Sufficient iron slurry was injected to achieve 2 to 5% metallic iron concentration in the soil. The iron was a commercially available iron powder that had been screened and size classified into a less than 50 mesh particle size range by the supplier (Connelly-GMP Inc., Chicago). No cleaning or other treatment of the iron was performed prior to injection.

A fourth area (XA2) was treated with SM/TESVE, but no polishing treatment was deployed. This area served as the experimental control.

Following preliminary analysis of the results of the performance monitoring samples, it was decided to perform further iron-addition experiments. These experiments (XA6 through XA10) were intended to confirm the results of the earlier experiment and to investigate several ways of integrating the iron addition with the SM/TESVE process. These supplemental experiments were performed in much the same way as the original, except that the amount of iron was reduced, and the amount of steam used and length of time spent steam stripping the soil varied.

Investigative Approach

The relative effectiveness of the three systems was monitored by measuring the effects on VOC concentrations over time. Other analyses were also performed to monitor the progress of the investigation. These included analysis of water samples from four wells and analysis of off-gas samples.

Prior to deploying the experiments, the initial conditions were assessed by performing a characterization of each experimental area prior to any treatment. Soil samples (pretreatment samples) were collected from each area to a depth of approximately 6 m (18 ft). The samples from each 0.6-m (2-ft) depth interval were analyzed first by field VOC screening. Selected samples were submitted for field VOC analysis in a mobile laboratory and confirmatory VOC analysis in a fixed laboratory. Other parameters, such as chloride and pH, were also measured prior to deployment of the polishing treatment systems.

Following the SM/TESVE treatment phase, an additional set of samples (initial characterization samples) was collected and analyzed in a similar manner. These samples represented the initial conditions for the polishing systems.

Once the three treatment systems and a control were deployed, the performance monitoring period was initiated. This consisted of the collection of soil core samples at periodic intervals and analysis of the samples for headspace organic vapor concentrations (field screening), VOC analysis in the field (mobile laboratory), and confirmatory VOC analysis in a conventional fixed laboratory. In addition, from time to time other parameters were measured in the soil, including pH, chloride, temperature, nutrients, methanol, and total iron concentration. Groundwater was sampled and analyzed on several occasions in several test areas equipped with groundwater monitoring wells. As discussed later, gas emanations were also captured and analyzed.

Sample collection continued until the target compound concentrations approached analytical detection limits, until no further changes were noted for three or more sampling periods, or until the approximately 90-day sampling period was completed.

Soil samples were collected using a push-point sampling device driven into the ground by a hydraulic sampling tool. Because of the extreme heterogeneity of the soil and contaminant characteristics, samples were selected from four depth intervals in each boring, typically 0 to 0.6, 1.2 to 1.8, 2.4 to 3.0, and 3.7 to 4.3 m (0, 2, 4, 6, 8, 10, and 12-14 ft) below the ground surface. Samples were consistently collected from near the bottom of each depth interval. The data from these four depths were then averaged to minimize the effects of heterogeneity.

ANALYTICAL METHODS

Field Organic Vapor Screening

Every soil core sample collected was screened for the presence of organic vapors with a field organic vapor analyzer (Microtip Model MP-1000 with a 10.6-eV lamp; Perkin-Elmer, Norwalk, CT). The soil was screened by measuring the amount of organic vapors in the headspace above soil placed in a sealed glass jar that had been heated to 32°C (90°F) in an oven.

Laboratory Methods

Most VOC analyses were performed by using a field analytical method 3810 (SW-846) (5). This method involves placing weighed amounts of soil into sealed glass vials, heating the vials to 90°C (194°F) with an autosampling device, and injecting the headspace gas into a gas chromatograph. The resulting chromatogram was then used to calculate the concentrations of VOCs in the soil. The precision, accuracy, and minimum detection limits for this method were evaluated with known quantities of contaminants added to clean sand. Detection limits were found to be approximately 0.1 mg/kg.

Occasionally, samples were split and part of the sample sent to an off-site analytical laboratory that performed VOC analysis by using the standard VOC analytical method (SW-846 Method 8260A) (5). The results of this comparison indicated that the field method was significantly more sensitive to VOCs than the laboratory method; the field method produced results typically around two times higher than the conventional method. All VOC results were reported on a dry-weight basis.

Whenever possible, standard EPA methods (5) were used for the other miscellaneous analyses.

RESULTS OF THE FIELD TRIAL

Average VOC concentrations in the soil prior to any treatment were as high as 125 mg/kg. Individual sample results included concentrations as high as 315 mg/kg. The most abundant contaminants were chloroform, carbon tetrachloride, trichloroethene, and tetrachloroethene. Several nonchlorinated organics were also present, including benzene, toluene, and xylene.

SOIL CONDITIONS FOLLOWING SM/TESVE TREATMENT

The SM/TESVE process was performed on each test area; varying amounts of time were spent mixing the soil. Table II compares average field VOC concentrations before and after SM/TESVE treatment and gives VOC removal efficiencies for the most significant contaminants. Removal efficiency varied significantly and ranged from 22 to 99%. Most of the removal values fell within the 75 to 95% range.

The SM/TESVE treatment was not performed prior to the supplemental iron-addition experiments XA6, XA7, XA8, XA9, and XA10. Consequently, no data are available on the effectiveness of SM/TESVE alone in these experiments.

The SM/TESVE process left the soil very wet: the moisture concentration increased from 10 to 12% to over 30%. The mixed area had the consistency of stiff mud. Several of the groundwater monitoring wells placed in the mixed soil contained water to within a meter of the surface, indicating that the majority of the mixed soil was saturated with groundwater already present, and with steam and water used to cool and lubricate the Kelly bar bearings.

RESULTS OF FIELD EVALUATIONS

Control

As anticipated, the VOC concentrations in the control area did not exhibit a noticeable trend during the experiment. The lack of a clear trend in VOC concentrations demonstrated that once the initial removal accomplished by the SM/TESVE process was achieved, no further reductions in VOC concentrations occurred.

Soil Ventilation Experiment

The VOC concentrations in the soil ventilation experiment did not decrease significantly during this experiment. The apparent inability of this system to reduce VOC concentrations is not surprising, given that the soil was saturated with groundwater starting several meters below the surface. The

Table II VOC Removal Efficiency following SM/TESVE Treatment

Constituent	Initial Concentration (mg/kg)	Final Concentration (mg/kg)	Removal Efficiency (%)
Carbon tetrachloride	125-5.1	21-<0.1	34-99
Chloroform	21.8-1.2	4.6-0.54	52-79
Tetrachloroethene	9.1-0.23	1.6-<0.1	82-83
Trichlorethene	60-7.8	8.0-1.47	55-88
4-Methyl-2-pentanone	2.6-0.52	2.17-0.37	22-81

groundwater filled the available pore space in the soil, thereby preventing the flow of air needed to carry away the volatile contaminants.

Two factors that prevented the soil ventilation system from working effectively were the high clay content of the soil and the fact that the version of the SM/TESVE process employed used steam to heat the soil, which added moisture to the mixed area. If the soil had been more permeable, the excess water would have drained away, which would have allowed more air to move through the pore spaces. With the high clay content in the 317 Area, this could not occur.

Augmented Biodegradation Experiment

The results of VOC measurements of this system indicate that no chlorinated or nonchlorinated organics that were absorbed onto the soil were destroyed. This was confirmed by the absence of an increase in chloride concentrations. Groundwater data indicated that some biodegradation may have occurred in the water phase; however, it did not occur fast enough to reduce the soil concentrations by the end of the study.

Biological assays of the soil indicated that in the early part of the study a bacterial population was present at levels that appeared to be higher than the control and increasing with time, and that the population was more diverse. However, within the time frame of this investigation, the bacterial population was apparently not able to metabolize large enough quantities of the contaminants to register a decreasing trend in VOC concentrations in the soil. It is possible that the length of the performance monitoring period for this study may have been too short to determine whether this is a viable technology.

Iron-Addition Experiments

In all the iron-addition experiments, most of the chlorinated compound concentrations (trichloroethane, chloroform, carbon tetrachloride, and 1,2-dichloroethene) showed rapid decline within the first few days after iron injection. The chloroform and carbon tetrachloride concentrations decreased to below the analytical detection limits (0.1 ppm) within several days of iron injection. The 1,2-dichloroethene disappeared within approximately 10 days of iron injection. The trichloroethane decreased more than 85% within 10 to 20 days. Tetrachloroethane, when present at high concentrations, showed rapid reduction within a few days; however, at low initial concentrations, less destruction was noted. Fig. IV shows the decline in selected VOC constituents in experiment XA7.

In experiment XA7, methylene chloride concentrations increased during the first 10 to 20 days of the experiment. Following this period, concentrations decreased. It is believed that the methylene chloride was produced by the dechlorination of carbon tetrachloride and chloroform. In experiments in which there was no carbon tetrachloride and chloroform, methylene chloride concentrations did not increase. This phenomenon has also been observed in other studies (8).

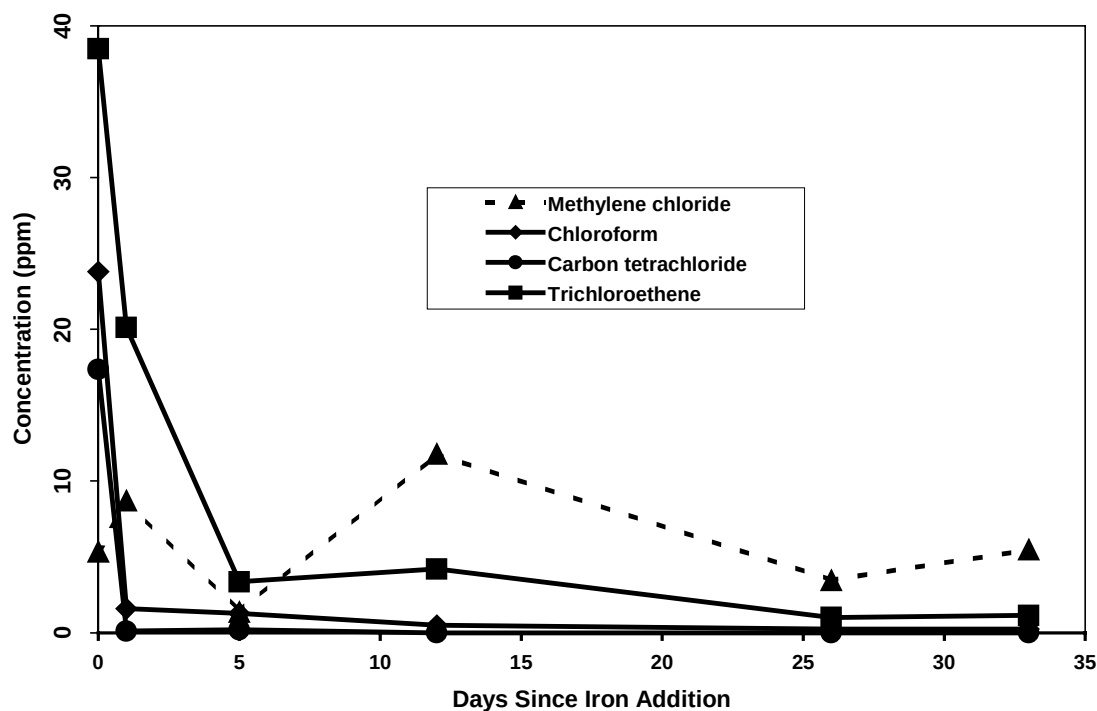


Fig. IV VOC Removal in Experiment XA7

Of the various combinations of iron and SM/TESVE treatment evaluated in these experiments, the most effective treatment was achieved with simultaneous injection of iron during the SM/TESVE process. This combination effectively reduced nonchlorinated organics because of the SM/TESVE process and effectively removed recalcitrant chlorinated organics through iron-mediated dechlorination. The combination resulted in lower residual VOC concentrations than the individual use of either approach.

After approximately 15 to 20 days, no additional reduction in VOC concentrations was observed in most of the iron experiments. The residual concentrations of chlorinated compounds at this point were low, often less than 1.0 ppm; in many cases, however, this amount of residual contamination still exceeded remediation objectives; thus, further reduction was needed. The reduction in effectiveness of the iron over time appears to have been related to a buildup of a precipitate on the outside of the iron particles and not to consumption (oxidation) of the iron itself. Examination of the soil following several months of treatment indicated that the mass of metallic iron was essentially unchanged. However, microscopic examination revealed that large amounts of the iron were coated with an unknown precipitate (9). This coating appears to interfere with movement of contaminants to the iron surface, where the reduction reaction occurs. However, further decrease in the residual concentration over long periods is possible because zero-valent iron is still present in the soil and the reaction could still be occurring, albeit at a lower rate. To determine whether this is the case, however, would require further study.

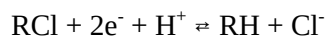
VOC concentrations in groundwater in the iron-treated area were much lower than in the other experimental areas, which indicates that the iron was removing VOCs from groundwater as well as the soil.

Concentrations of nonchlorinated organics (benzene, toluene, and 4-methyl-2-pentanone) did not demonstrate a trend, but remained essentially stable throughout the monitoring period. When the iron addition was integrated with the SM/TESVE process, these compounds were significantly reduced immediately after mixing, as were other petroleum products. These reductions were confirmed by a dramatic decrease in petroleum concentrations following the SM/TESVE process. However, following mixing, the concentrations of nonchlorinated compounds were generally stable compared with the chlorinated VOCs, which continued to decrease. This was as expected: iron is known to be effective only with chlorine-containing materials because the primary mode of reaction is an abiotic dechlorination reaction.

An increase in chloride concentrations in the soil was noted in the iron experiment. No increase was noted in the control or in the other experiments. Reaction products and intermediates were noted in some of the samples and included 1,2-dichloroethene and methylene chloride. Gaseous products of complete dechlorination (methane, ethane, propane, and butane) were also detected in the off-gas, which indicates that dechlorination was the primary means of destroying these compounds. Other reaction products, including hydrogen gas, were also detected.

During treatment significant quantities of gas (containing primarily hydrogen) were noted to be emanating at the surface; this gas was visible as bubbles coming up through puddles of water that formed over treated areas. Analysis of this off-gas for trace organics revealed the presence of up to several hundred ppmv of the same materials found in the soil. As it made its way to the surface, the off-gas carried with it significant concentrations of these compounds. Because the rate of gas generation from this system was very low and subsided within a few weeks of iron addition, the mass of materials carried from the soil by the off-gas was low—less than 1 to 20% of the mass originally present. However, the presence of these materials in the off-gas is important should a mass balance be attempted on this type of system. Because of the numerous sources of experimental error associated with this type of field deployment, no attempt was made to perform a mass balance on carbon or chlorine. Experiments in the controlled environment of a laboratory would be required to gather data of such quality that a mass balance would be meaningful.

The postulated degradation mechanism for iron treatment involves a reductive dechlorination reaction that sequentially removes chlorine from the hydrocarbon radical (R), and consumes hydrogen ions (resulting in a surplus of hydroxyl ions) that increase chloride ion concentrations and raise the pH (6-10):



A side reaction, not related to the presence of the organic contaminants, also occurs where free oxygen is absent:



This reaction generates gaseous hydrogen molecules as well as hydroxyl groups. Factors observed during this experiment, such as an increase in the soil pH, an increase in chloride, and the generation of hydrogen gas, were also consistent with this postulated degradation mechanism.

FULL-SCALE DEPLOYMENT

Following a review of the analytical results from the zero-valent iron polishing experiments, ANL-E evaluated the cost to treat the soils with the iron injection polishing treatment compared with the soil ventilation system. The review showed that treatment costs per unit of soil volume would be somewhat lower with the iron injection, and lower residual concentrations would result. After experimenting with various iron injection methods and evaluating the effects of iron on different contaminant mixtures, it was decided that iron treatment rather than soil ventilation would be used as the polishing step.

The integration of iron injection into the SM/TESVE process required significant modification of the treatment equipment, in addition to considerable effort to troubleshoot operational problems and improve the effectiveness of the system. For example, the efficiency of the iron injection method was found to be highly dependent on the degree of mixing and the moisture content of the soil at the time of injection. Once the process was refined, it was used to treat approximately 4,050 m³ (5,300 yd³) of contaminated soil.

Approximately 2% of iron by weight was added to the soil. The steam and air stripping occurred immediately before the iron slurry was pumped through the Kelly bars and into the soil. The augers then distributed the iron within the treatment column. Each treatment column, approximately 3.3 m² (35 ft²) and 7.3 m (24 ft) deep, was treated in approximately 90 minutes, compared with up to three hours for the SM/TESVE process alone. The rig would then remove the augers from the soil and relocate approximately 1.5 m (5 ft) away from the last treatment area. A new column would then be mixed. The columns overlapped approximately 10% to minimize any untreated soil lying between treatment areas. This process was repeated until the target area was treated.

The treatment was performed only in the areas within the 317 Area that exhibited the highest levels of contamination, that is, the hot spots. The hot spots represented the bulk of contamination of this area. The larger region of soil surrounding the hot spots, which contained much lower concentrations of VOCs, was not treated because it would not be cost effective.

RESULTS OF FULL-SCALE TREATMENT

Examination of the analytical data from the initial and final sampling of the treatment areas indicates that dramatic reductions in VOC concentrations were achieved. A comparison of field VOC screening results before and after the treatment process showed that essentially the entire main hot spot was removed, thereby reducing headspace VOC levels by 90 to 99% in most locations treated.

In many cases, the SM/TESVE process, augmented by iron addition, attained removal efficiencies of specific chlorinated organic compounds greater than 99%. The SM/TESVE process alone was able to achieve only 70 to 80 % removal of these compounds. Table III compares the removal efficiency of the SM/TESVE process alone with that of the integrated SM/TESVE with the iron-addition process.

CONCLUSION

Given the soil conditions naturally present in the 317 Area (high clay content with resultant low permeability) and the conditions created in the soil by the type of SM/TESVE process utilized in this project (steam injection that resulted in nearly saturated soil conditions), the only viable soil polishing treatment system of the three evaluated was the iron addition. The addition of 1 to 3% iron dramatically reduced residual VOC concentrations, compared with no polishing or polishing using the soil ventilation or the augmented biodegradation processes.

The data collected during this study indicate that the reduction in VOC concentrations was accomplished by dechlorination of the chlorinated solvents, which resulted in increased chloride ion concentrations. A much smaller amount of removal occurred because of volatilization of the organics into the gas emanations generated by the anaerobic oxidation of the iron particles.

The effectiveness of the iron addition varied significantly, depending on the compound being treated. The most amenable chlorinated compounds were chloroform, carbon tetrachloride, 1,2-dichloroethene, trichloroethene, and tetrachloroethene (at high concentrations). Methylene chloride was found to be generated as a relatively stable end product of the dechlorination of chloroform and carbon tetrachloride. However, there were indications that it too would have eventually been removed to very low levels over a longer time period than this experiment allowed.

Table III VOC Removal Efficiency following Full-Scale Treatment

Constituent	Range of Removal Efficiencies with SM/TESVE Only (%)	Range of Removal Efficiencies with SM/TESVE Augmented with Iron Addition (%)
Benzene	81-90	57-96
Carbon tetrachloride	34-99	100
Chloroform	52-79	99-100
Tetrachloroethene	83	84-99
Trichlorethene	55-87	96-100
4-Methyl-2-pentanone	21-81	87-99
Nitrobenzene	25-52	95
Total VOC ^a	30-45	99.6-99.8

^a Total of all VOCs except acetone and methylene chloride, which were lab contaminants.

The conclusion that iron addition is a viable soil polishing treatment system is likely to be very site specific. The effectiveness of the iron appears to depend on the presence of sufficient soil moisture to essentially saturate the soil. In addition, soil conditions must be such that the soil moisture stays in intimate contact with both the soil and the iron for extended periods of time (weeks to months). The low-permeability soil of the 317 Area provided these conditions. Other sites with higher permeability soil or in more arid locations may not be able to support such high moisture levels for the length of time necessary to see residual concentrations decrease to acceptable levels.

The iron addition did not prove effective at reducing the concentrations of nonchlorinated volatile organic species. However, concentrations of hydrocarbons identified as diesel fuel did decrease substantially in all test areas, most likely because of the initial SM/TESVE treatment where it was used.

RECOMMENDATIONS

This study determined that the injection of zero-valent iron is an effective enhancement to the SM/TESVE process for removing concentrations of VOCs from the soil in the 317 Area. However, the conclusions derived from this study are likely to be highly site specific. A better understanding of the effectiveness of this process under different conditions is warranted. The iron-addition process needs to be studied in a controlled environment so that the various factors contributing to its success or failure can be better understood. In addition, a better understanding of all mechanisms responsible for reducing VOC concentrations is needed. Because of the complexity of performing treatability studies in the field, laboratory-scale studies to identify treatment mechanisms and confirm the fate of the compounds are recommended. Only through such studies can the applicability of this technology to other sites with different soil conditions and different contaminants be assessed.

REFERENCES

1. ARGONNE NATIONAL LABORATORY, "Conceptual Design Report for the 317 Area French Drain (SWMU No. 11)" (1997)
2. ARGONNE NATIONAL LABORATORY, "Determination of Corrective Action Report for the 317 Area French Drain (SWMU No. 11)" (1997)
3. U.S. DEPARTMENT OF ENERGY, "In Situ Enhanced Soil Mixing," DOE/EM-0289, Office of Science and Technology (1996)
4. ARGONNE NATIONAL LABORATORY, "Resource Conservation and Recovery Act Facility Investigation Report 317/319/ENE Area" (1997)
5. U.S. ENVIRONMENTAL PROTECTION AGENCY, "Test Methods for Evaluating Solid Waste: Physical/Chemical Methods," EPA-SW-846, Office of Solid Waste (1986)
6. R. FOCHT, et al., "Field Application of Reactive Iron Walls for In-Situ Degradation of Volatile Organic Compounds in Groundwater," *Remediation* (1996)
7. L.J. MATHESON and P.G. TRATNYEK, "Reductive Dehalogenation of Chlorinated Methanes by Iron Metal," *Environmental Science & Technology* 28(12):2046 (1994)
8. W.S. ORTH and R.W. GILLHAM, "Dechlorination of Trichloroethene in Aqueous Solution Using Fe⁰," *Environmental Science & Technology* 30(1):66 71 (1996)

9. E.J. REARDON, "Anaerobic Corrosion of Granular Iron: Measurement and Interpretation of Hydrogen Evolution Rates," *Environmental Science & Technology* 29(12):2836 (1995)
10. K.D. WARREN, et al., "Kinetics and Mechanism of Reductive Dehalogenation of Carbon Tetrachloride Using Zero-Valence Metals," *Journal of Hazardous Materials* 41:217-227 (1995)