A COMPARISON OF IN SITU SOIL MIXING TREATMENTS

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ABSTRACT: A series of bench-scale tests were performed to determine the suitability of insitu soil mixing to treat clayey soils contaminated with chlorinated compounds and solvents at a site also used as a radioactive storage yard at Argonne National Laboratory-East near Chicago, Illinois. Soil mixing with hot air injection was proposed as the initial treatment and as the delivery system for a number of polishing techniques including zero valent metals, biological agents, potassium permanganate, humic acid, and soil vapor extraction. Batch tests were performed on soils samples using simulated soil mixing and hot air injection. Additional tests were performed on several polishing technique, after a portion of the volatile contaminates were removed by the hot air injection and soil mixing. The results were compared for removal efficiency and cost.

It was found that about 50 to 80% of the contaminate mass was removed by hot air injection. The polishing techniques were used to increase treatment efficiencies to 70 to 99%. Soil vapor extraction and zero valent metals (iron filings) treatments provided the greatest short- term treatment efficiency. Proprietary combinations of treatments such as biodegradation/zero valent metals and humic acid/biodegradation produced treatment efficiencies near 90% in about two weeks with the promise of continued improvement with additional time.

INTRODUCTION

The 317 Area French Drain had been used as a disposable area for waste fluids at the Argonne National Laboratory-East during the late 1950's, before current waste management practices were instituted. Workers previously poured liquid wastes into gravel filled trenches or into tanks where they slowly leaked into the soil. As a result, total volatile organic chemical (VOC) contamination in the soil was recorded as high as 3,500 mg/kg. The contamination was found up to 30 feet (9 m) deep over an area of about 1 acre (4000 m^2). The soils at the site are hard and impermeable glacial clays and till. The site is currently used as a staging area to temporarily store radioactive wastes prior to off-site disposal. A voluntary cleanup was designed to remediate the 317 Area.

Insitu soil mixing is a construction technique which has increasingly been relied upon for the remediation of contaminated soils. Depending on the application, large or small (4 to 0.3 m) mixing augers can be used to inject cement, bentonite or other reagents to modify soil properties and thereby remediate contaminated soils and sludges. A major advantage of the method is the capability to inject a variety of reagents and treat soils at depth (up to 35 m deep) without excavation, shoring or dewatering. Advantages of soil mixing over alternative technologies include lower cost, less exposure of wastes to the surface environment and eliminating off-site disposal. These advantages convinced Argonne National Laboratory-East to use a system of insitu soil mixing coupled with hot air injection, as shown in the sketch for the 317 Area soil remediation.

Process Diagram for Insitu Soil Mixing

In order to properly evaluate the potential success of soil mixing at a particular site it is generally advisable to conduct a pre-construction laboratory testing program to establish treatment capabilities, optimize reagent usage, and better define costs. Such a study was performed for the 317 Area project. The purpose of this study was to determine the total percentage of contaminates which could be removed.

METHODS AND MATERIALS

The methods and materials tested were selected to mimic field construction based on the author's previous experience, economic considerations, and local availability. The following materials were included in the testing:

MATERIAL	SOURCE
contaminated soil	samples from the site obtained via drilling
hot air (temperature = 100^{0}C)	laboratory generator
potassium permanganate	Carus Chemicals Co.
humic acid (Humasorb)	Arctech, Inc. (proprietary formulation)

iron filings	Peerless Metals, Inc.
biological/metals (Daramend)	W.R. Grace (proprietary formulation)
guar gum polymer	Rantec, Inc.
methanol	laboratory stock
formate	laboratory stock
phenol	laboratory stock

The testing was performed in a series of steps 1) first the contaminated materials were tested for total VOCs, 2) the contaminated soils were next treated with hot air injection and mixing for 30, 60, 90,and 120 minutes and retested, and 3) each of the polishing techniques was mixed with identical samples of the hot air treated soil and retested at various proportions and intervals.

The soils were tested for 28 different volatile compounds in accordance with EPA Method 8260A. Of the 28 volatile compounds only six had significant concentrations and these were carbon tetrachloride, chloroform, MIBK (4-methyl-2-pentanone), tetrachloroethene, 1,1,1 trichloroethane, and trichloroethene. Two other compounds, methyl chloride and vinyl chloride were also tracked during the testing due to a concern that some of the treatments could create these compounds if misapplied.

The efficiency of treatment was calculated for each compound and for the sum of the compounds as a "treatment efficiency". The specific compound treatment efficiency was calculated as follows:

$$\text{Specific Compound Treatment Efficiency} = 1 - \frac{\text{post-treatment concentration (mg/kg)}}{\text{pre-treatment concentration (mg/kg)}}$$

For the eight compounds previously discussed, an average treatment efficiency was calculated as follows:

$$\text{Average Treatment Efficiency} = 1 - \frac{\text{sum post-treatment concentration (mg/kg)}}{\text{sum pre-treatment concentration (mg/kg)}}$$

The higher the treatment efficiency the more contamination removed by the treatment. A method with a treatment efficiency of 100% removed all of the contamination.

RESULTS AND DISCUSSION

Soil Characterization. The untreated site soils exhibited significant contamination, especially with trichloroethene. A summary of test results on the untreated soil is reproduced in the table below.

Chemical Compound	Concentration (mg/kg)	Physical Properties	Result
Carbon Tetrachloride	22	PH	7.6
Chloroform	5.2	Moisture Content (%)	19
Methylene Chloride	0.4	Loss on Ignition (%)	2
MIBK	6.2	Unit Weight (kN/m^3)	21.0
Tetrachloroethene	160	% Gravel	3
1,1,1 Trichloroethane	7.6	% Sand	15
Trichloroethene	16	% Silt	38
Vinyl Chloride	0	% Clay	44
Total of 8 VOCs	217.4	Plastic Index (%)	16

Hot Air Treatment. The soils were treated by mixing and injecting hot air in an open container. About 2500 gm of soil were mixed in a modified laboratory-type blender at 60 rpm with hot air (100^0C) injected at 10 liters per minute. Samples of the treated soils were taken at intervals to evaluate VOC removal efficiency. After 90 minutes of mixing in the laboratory, a treatment efficiency of about 70% was obtained which is consistent with previous field experience for penetration and initial mixing of a large diameter soil column. Six duplicate batches were mixed and tested with typical results as shown in the table below.

Compound	Batch 2 (mg/kg)				Batch 4 (mg/kg)	Batch 5 (mg/kg)
Mixing Minutes→	**30**	**60**	**90**	**120**	**90**	**90**
Carbon Tetrachloride	21	22	18	18	13	12
Chloroform	1.4	1.4	0.81	0.74	0.7	0.57
Methylene Chloride	0	0	0	0	0	0
MIBK	4.3	2.9	2.6	2.2	2.3	1.8
Tetrachloroethene	58	48	39	38	33	30
1,1,1 Trichloroethane	1.7	1.8	1.4	1.7	1	1.2
Trichloroethene	8.8	8.1	5.1	4.6	4.4	3.2
Vinyl Chloride	0	0	0	0	0	0
Total of 8 VOCs	95.2	84.2	66.9	65.2	54.4	48.8
Treatment Efficency (%)	**56**	**61**	**69**	**70**	**75**	**77**

Notes: 1) 0 = not detected

2) Pre-treatment concentration = 217 mg/kg

Polishing Techniques. Six polishing techniques were used to treat the contaminated soil after hot air mixing and injection. A number of vendors participated in the study by providing materials, expertise, and in the case of W.R. Grace, active involvement in the laboratory mixing. The iron filings and Daramend materials are solids and therefore, were blended into a slurry using a water-guar gum solution to suspend and carry the solids for mixing with the soil. For the iron filings, a series of trial mixtures were made with progressively finer filings until the workable slurry was made composed of iron filings (finer than #50 sieve size), guar gum and water. Potassium permanagate (KMn04) was mixed into a solution with water at the solubility limit at about 5%. The Humasorb product is a thick solution and was usable without amendments. A formate solution was mixed with the soils to enchance biological activity. The tests were performed on mixtures which were blended and then stored in a dark, controlled atmosphere for 2 days to 2 weeks to model insitu conditions.

A summary of the results of the testing are presented in the table below:

Compound	**KMn04**	**SVE**	**Iron Filings**	**Humic Acid**	**DARA-MEND**	**Bio-Treat-ment**
Additive→	**10%**	**7 Days**	**5% & Guar**	**L-3**	**D92 & Guar**	**Formate Solution**
Carbon Tetrachloride	12	0	0.028	1.9	0.4	5.4
Chloroform	0.371	0.043	0.3	0.50	3.4	1.3
Methylene Chloride	0	0.15	0.063	0	0.041	0.058
MIBK	1.8	0.63	1.1	0.61	0.33	0.31
Tetrachloroethene	27	2.7	1.3	9.5	18	23
1,1,1 Trichloroethane	0.87	0.52	0	0.24	0.5	0.51
Trichloroethene	2.3	0.11	0.37	1.00	5	4.4
Vinyl Chloride	0	0	0	0	0	0
Total of 8 VOCs	44.6	4.15	3.16	13.75	27.67	34.98
Treatment Efficency (%)	**79**	**98**	**98**	**94**	**87**	**84**

Notes: 1) SVE = soil vapor extraction

The results shown above indicate that insitu soil mixing with hot air can be significantly improved by the use of polishing techniques. Workability concerns can be addressed by making slurries with water and guar gum that enhance the process and the treatment. While these results are encouraging, several of the techniques should show continued improvement as biological organisms continue to degrade the contaminates and these techniques include Daramend and humic acid.

Specific Compound Treatment Efficiency. In general, all of the compounds were reduced by the hot air and polishing treatments. Different treatments produced differing treatment efficiencies with specific compounds. For example, carbon tetrachloride was more difficult to treat with hot air injection and potassium permanganate but easily treated with soil vapor extraction and iron filings. Trichloroethene was the found in the largest concentration of the contaminants, but was reduced to low levels by all of the treatments. While not detected in the characterization of the untreated soils, very small concentrations (< 0.2 mg/kg) of methylene chloride were detected in all of the polishing treatments except potassium permanganate. No vinyl chloride was detected in any treatment. A summary of specific compound treatment efficiencies are shown in the table below.

	Specific Compound Treatment Efficiency (%)						
Compound	**Hot Air Only**	**KMn04**	**SVE**	**Iron Filings**	**Humic Acid**	**DARA-MEND**	**Bio-Treat-ment**
Carbon Tetrachloride	23	45	100	100	91	98	75
Chloroform	85	86	99	94	90	35	75
Methylene Chloride	0	0	0	0	0	0	0
MIBK	65	71	90	82	90	95	95
Tetrachloroethene	80	83	98	99	94	89	86
1,1,1 Trichloroethane	86	89	93	100	97	93	93
Trichloroethene	71	86	99	98	94	69	73
Vinyl Chloride	0	0	0	0	0	0	0

Notes: 1) 0% = no change in concentration
2) 100% = complete removal of compound

Comparative Costs. A cost analysis was performed using the data obtained, above, to estimate the cost of each of the different techniques. The cost comparison was based on treating 20,000 cubic yards (15,000 m^3) of contaminated soils. Each vendor was contacted and allowed to optimize the expected reagent usage and cost. A summary of the estimated costs are shown in the following table.

Technique	**Initial Mixing with Hot Air Cost ($/cy)**	**Polishing Cost ($/cy)**	**Total Cost ($/cy)**
Soil Vapor Extraction	30	45	**75**
Zero Valent Metals	30	65	**95**
Daramend	30	31	**61**
Humic Acid	30	58	**88**
KMn04	30	105	**135**

CONCLUSIONS

Insitu soil mixing can be used to remediate clayey soils with relatively high levels of VOC contamination. Hot air injection can be augmented with a number of highly effective polishing techniques to provide greater than 90% removal of volatile compounds. This type of remediation can be relatively inexpensive when compared to other methods.