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Title: IN SITU RF/MICROWAVE REMEDIATION OF SOIL  
EXPERIMENT OVERVIEW

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# IN SITU RF/MICROWAVE REMEDIATION OF SOIL EXPERIMENT OVERVIEW

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## ABSTRACT

Contaminant plumes are significant waste problems that require remediation in both the government and private sectors. We have developed an in situ process that uses RF/microwave stimulation to remove pollutants from contaminated soils. This process is more efficient than existing technologies, creates less secondary pollution, and is applicable to situations that are not amenable to treatment by existing technologies. Currently the most commonly used process is soil vapor extraction. However, even when it is successful, this technology is energy inefficient.<sup>1,2</sup> Our objective is to combine RF/microwave energy application with soil vapor extraction to help mobilize and efficiently remove the soil contaminants, specifically demonstrating the viability of RF/microwave induced, in situ, soil remediation of "light and dense non-aqueous phase liquids" (LNAPL, DNAPL) contaminants.

We have conducted a number of benchtop experiments involving RF/microwave energy deposition and vapor extraction on controlled contaminated soil samples with successful removal of the contaminants. This paper will describe the experimental hardware utilized, the experiments performed, the chemical analysis performed pre- and post- energy application, and results. In our experiments, two different halogenated liquids were used to contaminate the soil: carbon tetrachloride (CCl<sub>4</sub>) and 1,1,1-trichloroethane (TCE).

## I. INTRODUCTION

Initially soil characteristics were calculated through permittivity measurements. This work is described in reference 3. IITRI has also performed soil dielectric property calculations using network analyzer measurements.<sup>4</sup> However these measurements were based on the complex input impedance of the soil in a transmission line. Our method<sup>3</sup> differed from this by including measured transmission parameters of the sample as well. We chose to use the transmission method because

we were using electrically short samples of the soil and the reflection method has a strong phase sensitivity in its algorithm that would have been influenced by our sample size.<sup>5</sup>

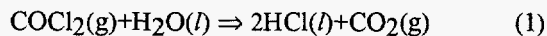
The experiments described herein comprise two parts. The main difference between the two is related to applicator design. The first set of experiments consisted of applying RF energy to a coaxial cavity packed with soil contaminated with a controlled amount of DNAPL. The next phase entailed designing a larger experimental chamber (2.5 gallons) with an antenna applicator to introduce the RF/microwave energy to the chamber. This setup more closely represents the envisioned application of RF/microwaves in situ in conjunction with vapor extraction. In the first phase, successful remediation in the 99% range of contaminant recovery was achieved, while in the second phase about 90% recovery was measured.

## II. PREPARATION & INSTRUMENTATION

### A. Preparing the Soil

Several different soils were used in the experiments. The soils originally examined included volcanic tuff, peat moss, indigenous dirt from Los Alamos National Laboratory and soil from an air force base (a possible end-user of the technology). The air force soil was utilized as the primary testing sample throughout the laboratory experiments. Each soil was prepared by removing any rocks and debris either mechanically with a Rototap or by hand with a flour sifter. In order to eliminate any possible reactions of the contaminants with water, initial tests were performed with dry soil. In the first phase, 300 to 400g of the fine soil were dried in a conventional oven at 60 to 80°C. The length of drying time varied from one to several days depending on the experimental run. In the second phase of the experiment, 6800 to 9800g of soil were dried in a larger oven at 80°C overnight. The mass of the dirt before and after heating was measured to record moisture loss in the soil.

Dry soil was important to eliminate specific health and safety concerns regarding the creation of phosgene. That is, if phosgene ( $\text{COCl}_2$ ) is produced from the decomposition of carbon tetrachloride, the product will further decompose into hydrochloric acid and carbon dioxide in the presence of water<sup>6</sup> as shown in equation 1. In this case the volatiles within the soil or in the vapor state would be lost.

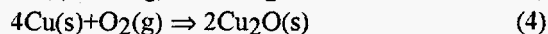
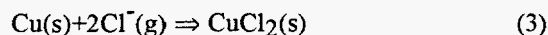


#### A. RF Source and Transmission System

The RF source was a 425 MHz, 200 W, continuous-wave amplifier, connected to the test chamber through a coaxial transmission line. A double stub tuner was used to minimize the reflected power throughout the experiments. Rate-monitored inlet air flowed through the contaminated soil and exited through an outlet port to various collection apparatus.

#### B. Microwave Chamber

1. Phase 1 Applicator. A portion of the coaxial transmission line was isolated using gas barriers and filled with contaminated soil; the output end was short-circuited. This portion was the phase 1 microwave "chamber." This copper chamber was coated with gold (see Figure 1). A gold coating was used to prevent reactions between the copper, the decomposed products of the plume, and the plume itself, as shown in equations 2 and 3. Also, the gold coating protected the copper metal from oxidizing with the heated air, as in equation 4.

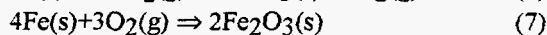
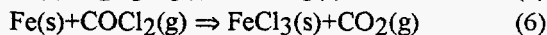


The flanges found at the ends of the chamber were sealed to prevent the flow of contaminants into the coaxial line outside the microwave chamber and corroding the surface. Air inlet and outlet ports on the chamber allowed for controlled stripping air flow. These ports were connected to the collection apparatus by stainless steel tubing and swagelock fittings. The stainless steel tubing was replaced several times throughout the experiment due to the reaction of the tubing with the plumes.

A thermocouple at the outer surface of the test sample (1/8" into the soil) monitored the soil temperature. By observing the soil temperature

we were able to maintain a RF power level adequate to heat the soil near the DNAPL's boiling point, but less than the boiling point of water.

2. Phase 2 Applicator. In the second phase of the experiment, a 2.5 gallon can was placed inside an 8 gallon drum as indicated in Figure 2. The 2.5 gallon steel chamber was also coated with gold to prevent reactions between the steel, the decomposed products of the plume, the plume itself, and oxidation from the heated air. The equations for reaction with iron are given below.



In equation 5, the stainless steel tubing will only be corroded by the plume itself in moderation when the volatile is dry. The corrosion increases if the water content increases. In equation 6, the reaction will only happen marginally even though there is an elevated temperature and air is present.<sup>7</sup>

The RF power was transmitted to the can chamber via a coaxial transmission line, then delivered through an antenna to the soil. The antenna was encased in a Teflon tube (1.5" inside diameter). The temperature of the soil was measured using thermocouples inserted 1/4" into the soil's outer surface, placed at different locations on the can chamber. Thermocouples 1 through 3 were placed radially from the center of the 2 1/2 gallon can to the outside edge. Thermocouple 4 measured the can's top surface temperature. Thermocouples 5 and 6 measured the temperature of the can laterally (1/3 and 2/3 of the distance from the top, respectively). Thermocouple 7 measured the temperature at the bottom of the can. The air flowed from the outside 8 gallon drum to the inner can chamber via 6 small openings distributed evenly around the bottom of the inner can. A vacuum was setup to extract the air through the contaminated soil through openings at the top of the Teflon well to the collection apparatus. As in the first phase, the collection apparatus was connected by stainless steel tubing. This more closely represents our envisioned application of in situ RF energy in conjunction with vapor phase extraction: a single applicator well in the center of the contaminated region used for both volume heating and extraction. The IITRI work relies on an array of electrodes placed in boreholes along the entire length of the contaminated area.<sup>8</sup>

### C. Collection Apparatus

1. First Phase Experiment. The collection apparatus consisting of water and dry ice/acetone baths was set up to capture the plume vapors after RF heating of the contaminated soil sample. The collection apparatus used in the first phase experiments is shown in Figure 1. The vapors were mobilized through the soil with air which was first dried with a dessicator. The extracted vapors were passed through a 2.5°C deionized water bath condenser where the contaminants were collected in a 100mL graduated cylinder. Any vapors that bypassed the first bath were further cooled down by a dry ice/acetone bath, at approximately -80°C. These plumes were captured in a 25mL impinger. In order to insure no unwanted vapor release into the air occurred, a water trap was placed at the end of the collection apparatus. The water trap was a 125mL filtering flask with 100mL of distilled water at room temperature. The pH of the water was tested with universal litmus paper before and after the experiments for the presence of unwanted contaminants.

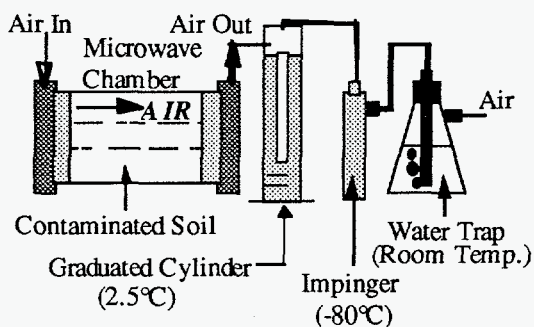


Figure 1. Phase I Collection Apparatus Diagram.

2. Second Phase Experiment. For the second phase of the experiment, the collection apparatus was expanded to include a 250mL impinger, a liquid nitrogen bath, a residual gas analyzer, an air trap, an air flow meter and a pressure gauge. The experimental setup used in the second phase of the experiment is shown in Figure 2. Because we increased the size of the chamber and the volume of contaminant, we chose to add a large impinger to our collection apparatus. Both impingers were submerged in liquid nitrogen, at approximately -195°C. The residual gas analyzer (RGA) was placed after the liquid nitrogen bath to test for any vapors carried by the air flow that were not captured by the collection apparatus. The RGA was also used to detect if any dioxins were being produced or escaping into the vacuum pump. The air trap

placed after the water trap prevented any water from entering the cryogenic pump. The air flow meter controlled the rate of air flowing through the tubing of the collection apparatus, and the pressure gauge was included with the cryogenic pump.

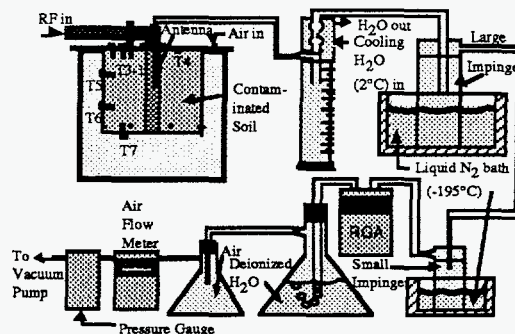


Fig. 2. Phase II Collection Apparatus Diagram.

### III. METHOD OF OPERATION

#### A. First Phase Experiment

The mass of the glassware for the collection apparatus was measured. Then, the test chamber was cleaned with ethanol to remove contaminants. Glass wool was added to one end of the chamber for packing purposes. The soil sample was then added to the chamber with the thermocouple opening sealed and another piece of glass wool added for cover. The chamber was then closed and attached to the rest of the microwave circuit. Initially, the carbon tetrachloride or the 1,1,1-trichloroethane was manually mixed with the soil before placement in the chamber. Since the volatiles evaporated when mixed, an accurate final reading of the amount of contaminants used in the experiment could not be obtained. Ultimately, the contaminants were injected into the soil through the thermocouple port. The amount of volatile used was 20 to 24 mL per experiment.

Once everything was connected, the initial temperature was measured. The experiment was started with the RF amplifier, the air flow, and the stopwatch turned on concurrently. The air flow was controlled with a needle valve located before the dessicator. The air flow was not measured quantitatively but was monitored by observing the amount of air bubbles produced in the water trap, approximately 4 to 5 bubbles per second. The initial power delivered to the contaminated soil was 70 watts. The chamber was covered with foam for insulation. When the amount of  $\text{CCl}_4$  or TCE collected was leveled for

20 minutes the experiment was stopped. After the RF power was turned off, the impinger was disconnected from the collection apparatus and the mass was measured. The collection apparatus was left to cool. The graduated cylinder and the soil in the chamber were also measured. The amount of plume collected in the graduated cylinder was converted to grams from its density value (1.5940g/mL for carbon tetrachloride and 1.3390g/mL for 1,1,1-trichloroethane).

After dry soil experiments were completed, a baseline experiment was conducted to measure the amount of volatile collected in the impinger and the graduated cylinder due to air stripping alone. The same procedure was followed for the RF heating experiments except no microwave energy was applied to the chamber. The experiment ran for 3 hours to monitor any major changes occurring within that time frame.

Since most contaminated soil contains some amount of moisture, the next set of experiments involved the introduction of water to the soil in controlled amounts. The ratio of water used was 20, 50, 60, 70 and 80% by mass of soil present in the experiment. The same volume of volatiles used in the dry soil runs was injected into the wet soil sample through the thermocouple port and the same procedure was followed. The only difference in these experiments was the power applied. The three power levels used in these experiments were 70, 100 and 130 watts.

#### B. Second Phase Experiment

The second phase of the experiment followed the same procedure with some differences. In the inner can, the glass wool was used to cover the openings at the bottom of the inner can to prevent any plume from leaking into the larger drum. The well of the antenna was set first before the soil was added. Once the chamber was sealed, it was insulated with 2" fiberglass on top. The surrounding tubing and instrumentation were insulated to maintain the high temperature to the graduated cylinder before condensation of the plume began. The 1,1,1-trichloroethane (TCE) was injected into the soil through a thermocouple port (port 2). Carbon tetrachloride was not used in this phase of the experiment since it was banned from Laboratory use between the start of the experiments and this point in time. The amount of volatile used was 100mL. The same procedure was followed as the first phase where the initial temperature and initial conditions of

the apparatus were taken into account. The initial power delivered to the contaminated soil was 170 watts. After the amount of TCE collected leveled off, the RF was turned off, the impingers were disconnected from the collection apparatus, and the mass measured. The graduated cylinder and the soil in the can chamber were also measured. The amount of the contaminants collected in the graduated cylinder was again converted to grams from the density value.

Similar to the first phase, follow-on experiments involved the addition of water to the soil. The ratio of water used was 5, 10, 15, 20 and 25% by mass of soil present in the experiment. The power used at these levels was 175, 180, 185, 190 and 195 watts, respectively. The same procedure as the dry phase 2 soil experiments was performed with the same amount of TCE injected through the thermocouple port.

## IV. RESULTS

### A. First Phase Experiment

In the first phase of the experiment, 99.6% of the carbon tetrachloride and 97% of the 1,1,1-trichloroethane was recovered from the dry soil. The data obtained from the dry experiments with two types of soil are plotted in Figures 3 - 6. In the case of the trichloroethane, the recovery would have been higher but the bottle contains 1 to 4% dioxane as a stabilizer. If the dioxane was not present, then the percentage of the TCE recovered would have been higher but, as a consequence, the TCE would dehydrochlorinate first before any recovery of the plume is feasible.<sup>6</sup>

In the water saturated soil experiments, as the amount of water was increased, the amount of carbon tetrachloride recovered decreased. The graph in figure 7 shows the three different power levels with percentage volume recovered of carbon tetrachloride against the mass of water percentage. As intuitively expected, as the applied power level increased, the amount of contaminant recovered increased.

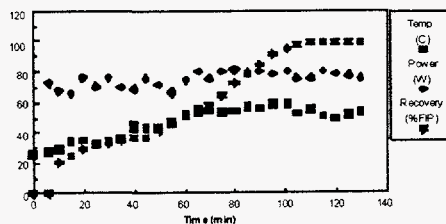


Figure 3. Phase 1 air force base soil with CCL<sub>4</sub>.

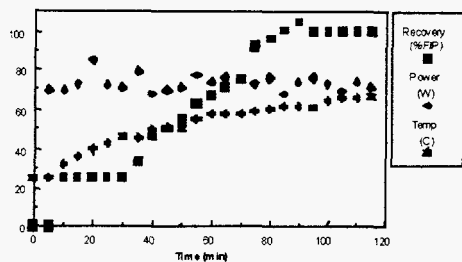


Figure 4. Phase 1 indigenous soil from Los Alamos National Laboratory with carbon tetrachloride.

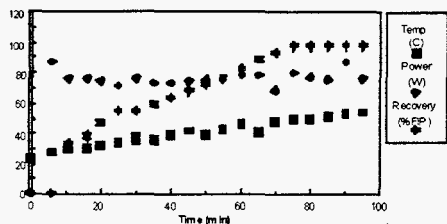


Figure 5. Phase 1 air force base soil with 1,1,1-trichloroethane.

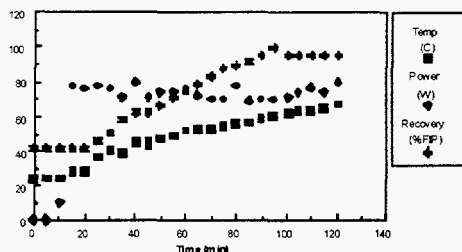


Figure 6. Phase 1 LANL indigenous soil with 1,1,1-trichloroethane.

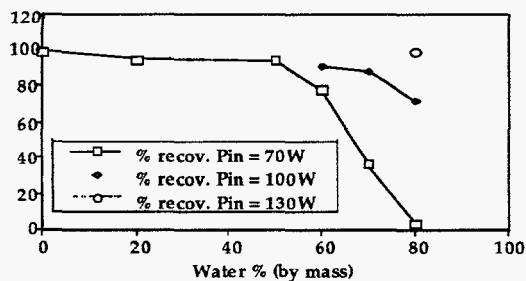


Figure 7. Phase 1 moisture content experiment with the air force base soil and carbon tetrachloride.

In the air stripping alone experiment, 16.6% of the carbon tetrachloride was recovered from the soil. All of the volatile was collected in the impinger. The temperature of the chamber did

not exceed 24.6°C, the initial temperature of the chamber. This experiment's data are plotted in Figure 8.

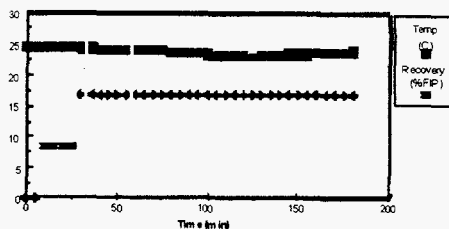


Figure 8. Baseline air stripping experiment with air force base soil and carbon tetrachloride.

This baseline experiment verified our premise that application of RF energy enhances vapor extraction.

### B. Second Phase Experiment

In the second phase of the experiment, about 90% of the 1,1,1-trichloroethane was recovered from the dry soil. A plot of the experimental data for an experiment on predried air force base soil with 170 W delivered power is given in Figure 9.

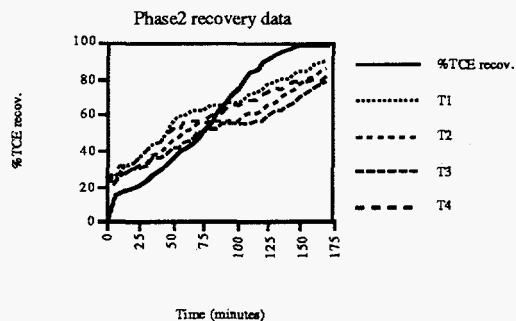


Figure 9. Plot of a Phase 2 experiment data using 170 W RF power delivered to 9.75 Kg of predried air force base soil.

### B.1 Measurement Problems Encountered

The percentage recovery was affected when sampling the gas by the residual gas analyzer (RGA). As the valves were opened to scan the volatiles present by the RGA, the tubing was filled up with the gas. The amount of TCE was not taken into account with the mass recovery in the impingers or the graduated cylinder. It also became a problem in performing sequential experiments because the tubing had the residual TCE from the previous sample. To remove the TCE from the tubing, it had to be baked out overnight with heat tape. Another problem was the air flow. The cryogenic pump was used to draw the air through the system thereby better

simulating vapor extraction methodology. A summary of the Phase 2 experiments performed is given in Table 1.

RF Power (W)	H <sub>2</sub> O % by mass	%TCE recovered
170	0 (dry)	91.0
170	0 (dry)	98.1
175	5	91.1
180	10	76.4
185	15	88.7
190	20	73.9
195	25	92.3
200	30	94.5

Table 1. Summary of Phase 2 experiments.

## V. CONCLUSIONS

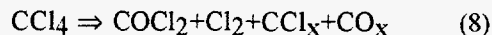
The recovery of carbon tetrachloride and 1,1,1-trichloroethane was very successful. In both the dry soil experiments and the water saturated soil experiments, the impinger initially frosted, then the graduated cylinder began to collect the volatiles. When the impinger frosted, the chamber of the microwave instrument was not hot. The impinger collection signifies that initial recovery was due to the initial air stripping. Once the vapors were heated, the water bath was cold enough to cool the plumes and condensation occurred.

While collecting the plumes from the soil, it was noticed that initially the boiling temperatures of the contaminants had not been reached at the thermocouple, although increased contaminant collection was occurring. Early experiments using volcanic tuff samples produced obsidian in certain areas of the microwave chamber due to localized heating. In the same manner, it is probable that local hot spots also occurred when the other soils were used, thereby helping the volatiles to evaporate at seemingly overall lower temperatures.

The water saturated soil experiments indicated that as the moisture content in the soil was increased and the power was kept constant, the amount of contaminant collected decreased. In order to collect a good yield, the power was raised. As the results showed, the percentage of contaminant collected was proportional to the amount of power supplied.

A secondary collection technique that was discovered during the procedure of this experiment was thermal decomposition of the carbon tetrachloride and collecting the plumes via

a water trap. When the power was ramped up to 300 watts, carbon tetrachloride decomposed to phosgene, chlorine gas, and chlorides and oxides of carbon, as shown below.



The pH of the distilled water in the water trap went from 7 to 1. Phosgene decomposes upon contact with water to hydrochloric acid and carbon dioxide. (eqn. 1) If the mobilization of the contaminant vapors cannot be captured in their respective state, then the plumes can be decomposed. The different components can be collected and disposed of properly.

## ACKNOWLEDGMENTS

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