SOIL REMEDIATION BY SURFACE HEATING AND VACUUM EXTRACTION

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ABSTRACT

A novel *in-situ*, thermal-vacuum method has been developed to remove contaminants from near-surface soils and pavements. Heat is supplied to the soil by downward conduction from a surface heater. Vaporized products are collected under an impermeable sheet into a vacuum system for further treatment or disposal.

INTRODUCTION

The contamination of soils by toxic, carcinogenic or radioactive materials, has become a matter of great concern at many locations throughout the world. In the U.S. alone, experts estimate that ten thousand sites eventually may require remediation. Since the enactment of the Superfund legislation in 1980, only a small fraction of the sites have been partially cleaned at a staggering cost approaching $10 billion.

Shallow contamination of soil, and of paved surfaces, by persistent chemicals is an especially widespread problem. Frequently, chemical compounds are spilled or placed on the surface of soils for dust or weed control, or for other agricultural purposes. Under these circumstances, the materials are often spread over very large areas. If the chemicals are judged to be detrimental to human health, or need to be dealt with for other reasons, the task of removing them or remediating the site is formidable. If the contaminating chemicals are sufficiently insoluble in water, they will not be leached into the soil by downward percolating rainwater, but will remain very near the surface for many years. Even with agricultural activities, such as plowing, disking, and harrowing, these contaminants are seldom carried as deep as a foot, and usually remain in the upper few inches of the soil.

The most direct method of remediating a shallow, contaminated site is simply to remove the soil by digging it up and carrying it to a disposal site; however, disturbance in the soil during the excavation always produces dispersion and secondary contamination. When dry, this occurs by windblown dust, and when wet, by rutting and other deep mixing of the soil. Because excavation with large equipment can spread the contamination into the soil, additional clean soil must be taken to assure complete removal of the contaminants. Furthermore, the transport of the hazardous waste to another location does not solve the overall problem, since the new site remains a potential problem and a continuing liability to the operators.

Most other methods that have been proposed to destroy contaminants also require: (1) excavation, (2) transport to a treatment facility, (3) some other means of destruction or removal from the soil, and (4) finally return of the soil to the original location. All of these methods suffer the hazards of secondary contamination from handling large amounts of material during excavations and process plant operations, such as incineration.

Methods that involve bioremediation or treatment of the soils by some kind of chemical washing have not proven to be sufficiently effective in removing chemicals to the extremely low levels of residual concentration required when highly toxic or carcinogenic compounds are present.

In U.S. Patent No. 4,984,594, Vinegar and Stegemeier[1] proposed a method using surface heating and vacuum extraction that avoids excavation by heating the soil *in-situ* to remove contaminants. Other desirable characteristics of this method are: (1) applicability for wide-spread, near-surface contamination; (2) effectiveness for a wide range of contaminants (even those with boiling points substantially greater than that of water); (3) ability to reduce the contamination down to very low levels; and (4) ease of operation for rapid and inexpensive remediation with a wide variety of soils and surface conditions. The volatile substances in the soil are vaporized by the heat, drawn upward, and gathered into a vacuum system where they are condensed in traps for subsequent treatment (e.g. incineration) or for disposal. Soil heating may be effected by means of an areal electric heater that is placed directly on the soil surface. The heater described in this initial patent is a mesh of electrically conductive wires. Heat is transferred by thermal conduction into the soil. A more durable heater, has been proposed by van Egmond, et. al. in U. S. Patent No. 5,229,583[2]. This heater consists of a metallic furnace belt with tubular electric heating elements inserted between the rungs of the belt. Compared with the previous design, the furnace belt (1) allows the heater to be rolled or dragged from one location to another, (2) provides a highly permeable path for vapor flow, and (3) distributes heat laterally between the heating elements. Another heater blanket design, U. S. Patent No. 5,221,827, by Marsden, Dicks, et. al.[3] incorporates a ceramic beaded conductive wire heater with a rigid stainless steel support frame. For uneven surfaces, a radiant heater design has been proposed[4] to provide good heat transfer into the soil even when the heater does not touch the soil surface. This later design is advantageous for large-scale applications, where improved thermal efficiency and ease of movement become more important.

During the past five years, the surface heater process has been studied in laboratory experiments and in pilot scale field demonstrations. Beginning in 1989, a series of field experiments with 10' x 10' heaters confirmed that an intermediate volatility hydrocarbon, normal hexadecane, could be effectively removed from near surface test soils. More recently, General Electric Company, using this patented process, has demonstrated the effective removal of polychlorinated biphenol (PCB) from a contaminated site at South Glens Falls, New York.[5,6] The process has been approved by the New York State Department of Environmental Conservation for development at the site, and plans are currently underway for full scale field operations in 1995.

PROCESS DESCRIPTION

General

Surface heating and vacuum extraction is an *in-situ* process for removing contaminants from surface and near-surface soils. Decontamination is achieved by evacuating the soil under a flexible, impermeable sheet, and heating the soil surface up to as much as 1000 C with a relatively flat electric blanket heater. (See Figures 1 and 2.) The heat flows downward by radiation and thermal conduction, and the consequent increase in soil temperature results in removal of contaminants by a number of mechanisms, including: vaporization, evaporation, steam distillation, pyrolysis, oxidation, and other chemical reactions. Contaminant vapors or volatile decomposition products are convected by the vacuum to the surface where they freely pass through the heater and a coplanar, high-permeability mat, to a vacuum port in the flexible sheet. The port is connected to a vacuum system that may contain: (1) cold traps for collection of the liquids, (2) adsorbers for collection of gases, or (3) thermal reactors through which the product stream may be passed for further destruction by oxidization or pyrolysis. At remediation sites where a large amount of water vapor is produced, it may be preferable to maintain vapor phase throughout the vacuum system and avoid trapping liquids. Differential pressure, between the atmosphere above the flexible sheet and the vacuum under the sheet, presses the sheet, mat, and heater firmly against the soil. This improves conformance with the surface and increases thermal contact of the heater with the soil. The impermeable sheet may extend areally beyond the surface heater and mat. In this peripheral region, the vacuum seals the sheet directly against the soil. Thus, the air, moisture, and contaminants in the soil below the heater are pulled almost vertically to the surface. Atmospheric air, which enters the soil from outside the impermeable sheet, is also produced. Outside air flow into the central vacuum system is restricted,

however, since it must travel some distance horizontally through the soil. (See Figure 3). The flow of air through the high temperature soil serves to evaporate and oxidize contaminants *in-situ*, thereby supplementing the vaporization and steam distillation mechanisms.

The method is potentially applicable to any compound that can be vaporized by boiling or evaporation, or to any compound that can be pyrolized or oxidized to form volatile products. Such compounds include most common industrial organic compounds such as pesticides, insecticides, chlorinated solvents, fertilizers, fuels, lube oils, and other non-aqueous phase liquids (NAPLs).

Equipment

Equipment and mode of operation have changed with type of remediation site and with advances in the technology. At a typical remediation site, the soil surface is prepared by removing rocks and vegetation and smoothing any irregularities that may be present. An electric resistance heater is placed directly on the ground. The areal extent of this heater will depend on the size of a particular site but could extend to greater than 50' x 50'. Several types of heaters have been considered, including uninsulated wire mesh, uninsulated bare nichrome wire, metal wires woven into a high temperature ceramic fiber cloth, and the more conventional MgO-insulated tubular, "cal-rod", heating elements. Heaters operated in the radiant temperature region will minimize heating time; however, at temperatures in excess of 850 C the heaters encounter severe corrosion in the soil environment. Sheath alloys such as Inconel 600, 601, or 602CA are effective in these high temperature applications. Electrical power may be supplied to the heaters at ordinary 60 Hz power-line frequencies with either single-phase or 3-phase configurations.

Depending on the type of heater design, a permeable layer may be constructed above, below, or may be incorporated into the heater. This layer is made of loosely woven wire, furnace belting, or similar spacing materials. The high permeability of this layer, relative to the subsurface soil, provides a nearly uniform pressure at the soil surface over the areal extent of the heater.

A thermal insulation layer, composed of ceramic cloths and woven fiber, or of loose vermiculite particles, covers the permeable layer and extends several inches beyond the heater. This insulation layer reduces vertical heat losses. In designs with a plastic flexible sheet, the insulation also protects the sheet from high temperatures. The thickness of this layer typically is from 2" to 12".

In the initial designs, a flexible sheet of fiberglass-reinforced silicone rubber, about 1/8" thick, was placed above the insulation and provided the vacuum seal. The sheet extended areally several feet beyond the heater to seal with the soil surface. The silicone rubber has excellent corrosion resistance but is rated for only about 270 C continuous service. Therefore, care must be taken to prevent overheating from the nearby heater. Alternatively, the surface vacuum seal might consist of a thin, sheet-metal cover over the heater, with either a vertical edge buried into the soil, or a silicone rubber skirt at the periphery to effect the soil seal. In that case, the thermal insulation is placed above the metal sheet, external to the vacuum.

For large sized impermeable sheets, more than one vacuum port may be needed to provide adequate vapor flow and to equalize pressures under the sheet. The vacuum lines from the sheet to the collection system may be heated to prevent condensation in transit. In most cases, a large volume of water vapor will be collected compared to the volume of contaminants and decomposition products. These vapors can be separated from the non-condensable gases and collected in a cold trap or in a cyclone separator located between the opening in the impermeable sheet and the vacuum pump. Trapped liquid or solid contaminants can be separated from water and transported for disposal or reuse at a disposal facility. Vapor phase contaminants and decomposition products can be trapped and concentrated on molecular sieve material, on activated carbon, or in a wet scrubber. If the contaminants are either incinerated in-line, or decomposed in thermal reactors, the entire downstream vacuum collection system may be maintained at a temperature slightly above 100 C and the water vapor vented into the atmosphere.

Operations

With the heater blanket and vacuum system in place, remediation is initiated by imposing a vacuum on the cold soil through the manifold connected to the impermeable sheet. If the surface is smooth, the vacuum will cause the sheet to be sucked tightly to the ground surface. If not, it may be necessary to add loose soil, clay, or weights at the edge of the sheet to improve the seal. In clayey or other low permeability soils, a

high vacuum can be obtained, whereas in highly permeable soils a lesser vacuum will occur, even if the impermeable sheet is extended. Usually, the amount of air pulled into the vacuum system will be large compared to the amount of in-situ contaminants. It is important to maintain the upward and inward flow rate of gases from the soil high enough to counter diffusive dispersion of contaminants or downward transport from vaporization and condensation; yet, flow rates that are too high will reduce the downward propagation of temperature from the heater and result in unacceptably long remediation times.

After a stable airflow rate is established by the vacuum system, the surface heater is energized and its heater temperature is allowed to increase to the maximum allowed for the heater design. Typically, this will be between 800 C and 1000 C. Heating at the maximum temperature is continued for a period of time ranging from several hours to several days, depending on the depth of contamination, type of contaminant, presence of ground water, and allowable residual at the end of treatment. Alternately, lower heater temperatures can be used for longer periods of time. In the case of very large areal heaters completely covering a contaminated site, it may even be feasible to evacuate an area and heat it mildly for many weeks. During heating, the thermal front moves downward into the soil by thermal conduction. This results in vaporization of water and contaminants in the near surface soil. The vacuum increases vaporization and causes boiling to occur at a somewhat lower temperature than the normal boiling point at atmospheric pressure. See Figure 4.

The presence of water, typically about 5% by weight in the soil, will enhance the removal of high boiling point contaminants by steam distillation. This occurs for all contaminants that are nearly immiscible in water, since the boiling point of a mixture of the two immiscible fluids is always less than the boiling point of either component. Thus, the normal boiling point of a mixture of water and dodecane is only very slightly below 100^{o}C, even though the normal boiling point of dodecane is 215 C. With steam distillation, even contaminants whose boiling points are well above 300 C can thus be vaporized. Water may be added to the soil to improve steam distillation; however, it is advantageous to minimize the amount, since the cost of heating and vaporizing moisture in most soils is greater than the cost of heating the inorganic minerals. See Figure 5.

For contaminants that are subject to thermal decomposition, at least a portion of the soil will be heated to a temperature sufficient to pyrolyze contaminants. In addition to decomposition of contaminants by pyrolysis, high temperature oxidation by the outside air that is drawn into the heated region largely breaks down hydrocarbons into CO_2 and H_2O, and chlorinated hydrocarbons into CO_2, H_2O and HCl. Vaporous contaminants that have not been pyrolyzed or oxidized deep in the soil are likely to react as they are drawn into the very high temperature soil immediately below the surface heater (about 800 C).

The treatment is terminated by switching-off the heater and allowing the soil to cool before the vacuum pumps are shut down. This assures containment of any residual contaminant at the fringe of the treated area. Nearly complete removal of a contaminant occurs at soil locations where temperatures reach either its boiling point or its decomposition point.

EXPERIMENTAL PROGRAM

A program of laboratory experiments, numerical simulations, equipment design, and field testing of the process was carried out to test the fundamental process premises, to develop equipment designs, and to demonstrate the efficacy of remediation.

Preliminary Studies

Literature data was collected and laboratory studies were performed to obtain vapor pressure of various contaminants as a function of temperature. Some compounds studied include: polychlorinated biphenols (PCB), cyclochlorodienes (CCD), and hydrocarbons having similar volatility, such as normal dodecane (n-$C_{12}H_{26}$), and normal hexadecane (n-$C_{16}H_{34}$). Volatility measurements at atmospheric pressure confirmed that vaporization or decomposition of all of these compounds occur at less than 300 C. See Fig. 4. Other bottle tests in ovens investigated the removal of contaminants from sandy soils. The presence of moisture and air were shown to lower the temperature required and improve the removal rate of the contaminants.

The thermal and fluid-flow aspects of the process were tested on a small scale in a series of sandbox experiments. A 304 stainless steel, wire-mesh heater, 6" x 6", was placed on the sand surface, blanketed with a layer of thermal insulation, and covered with a flexible silicone rubber sheet. A vacuum was drawn through a central port in the sheet. These tests demonstrated (1) that without peripheral sealing, the sheets could be sucked tightly against the surface of even high permeability sands; (2) that a wire mesh heater could easily heat the surface to 800 C; and (3) that the rubber sheet could be protected from the intense heat by relatively thin ceramic fiber insulation. Corrosion of these heaters appeared to be acceptably low in these relatively short time experiments with a clean, white, silica sand (Clemtex). Later more realistic experiments with natural river sand and over longer times revealed that better heaters would be required; however, the wire mesh heater enabled a 65 hour heat in the first pilot scale test (GRUF-#1) of the full process.

Numerical simulations of a small field pilot were carried out using a thermal simulator for underground fluid flow processes. These simulations predicted that the process would remove contaminants from the soil near the surface in reasonable times. For contaminants less than three feet deep in dry soil, the remediation could be carried out in less than ten days, and for contaminants less than one foot, in about one day. Predicted production rates of water, air, and contaminants, and heat flow rates, assisted in sizing of vacuum collection equipment and heaters, and in planning the conduct of a field test.

FIELD TESTS

Object

Based upon these laboratory experiments and design studies, a series of 10'x10' heater experiments was carried out to: 1) confirm that large scale soil heating takes place as predicted by lab models and numerical simulation, (2) confirm that a vacuum can be applied effectively to this size model, (3) establish the level of remediation that can be attained in the subsurface soil, and (4) optimize process variables. Besides process studies, the large scale experiments provided a means to test: (1) the operational capabilities and durability of the heater designs, (2) the effectiveness of the insulating layer and the thickness of insulation required, (3) the performance and practicality of the flexible silicone rubber sheet, and (4) the electrical power distribution and monitoring equipment. These experiments also provided an opportunity to learn how to practice safe electrical heating and vacuum procedures that can be followed in a field application of this high temperature process. Because these experiments were a combination of precise scientific measurements, together with operations with large scale practical equipment, a mixture of units has been used to avoid inconvenient descriptions of familiar measurements and observations.

Gasmer Road Underground Facility (GRUF)

The test site for the 10'x10' field experiments was located at Shell's Gasmer Road test facility in Houston, Texas. See Figure 6. An area 40' x 40' was enclosed by a 6' cedar fence to secure the test area. A 30' x 30' x 2.5' volume of the original heavy gumbo soil was removed and replaced with Brazos River sand. Sieve analysis shows this to be a fine, well-sorted sand with an average grain size about 0.005". Permeability is estimated to be about 5 darcys. At the surface in the center of the test area, a 10' x 10' x 1.5' volume of sand was "contaminated" with a non-toxic hydrocarbon, normal hexadecane, ($n\text{-}C_{16}H_{34}$). The hexadecane (B.P. = 287.56 C) has an intermediate volatility compared to some of the common chlorinated hydrocarbons, but it is much less volatile than water. Care was taken to mix the hexadecane uniformly by adding a small measured volume of heavily "contaminated" sand to an 8 cu. ft. mortar mixer. When each batch was thoroughly mixed, the sand was layered and compacted into the 10' x 10' area to a bulk density of about 1.5 gms/cm^3. A total of 90 soil samples were taken at 15 locations during the packing. These samples showed an average hexadecane concentration of 812 mg/kg sand, with a standard deviation of less than 50 mg/kg. Post-heating soil samples, taken by coring, were analyzed to evaluate the efficiency of the remediation. An external control hole, about 13.5' distant from the southeast corner of the heated region was filled with the "contaminated" sand, as a check on the survival of hexadecane in the unheated sand. No change was observed in hexadecane content in the control hole over a period of more than six months.

Heater Blanket

Heater blanket designs have evolved as a result of experiences in this series of field tests. Initial heating elements were bare wire stainless steel mesh or parallel nichrome wires placed directly on the soil surface. Later, mineral-insulated tubular elements and radiant heater designs have improved reliability and strength; however, because the initial experiment, with a wire mesh heater, had the most complete instrumentation, sampling, and measurements, it best demonstrates the process and will be described in detail below.

In this first soil remediation test (GRUF #1), a 10'x10' electrical heating element was constructed from 325 mesh, 304 stainless steel, with 0.0014" diameter wires arranged in four-2.5' x 10' strips in series. The heater is described as a "single-phase, M-4, N-9600," where M refers to the number of series and N to the number of parallel connections, in the spacing of wire element combinations on the soil surface. Total resistance of this heater at elevated temperature was about 1.3 ohms. The adjacent strips were separated by a 1" space and pegged to the ground to prevent movement. Strips were connected to each other by spot-welded stainless steel bus-bars. Copper power cables were bolted to the bus-bars at locations outside the heated zone.

Above the surface heater, a multilayered sandwich of permeable mats and insulation was placed to provide a conduit for horizontal flow under the impermeable sheet, and to protect the sheet from the high heater temperatures. The successive layers above the heater were: (1) a Nextel 312 (AF-14) alumina-boria-silica coarse cloth with 1 to 2 mm opening next to the heater; (2) corrugated 304 stainless steel knitted wire mesh, 0.011" x 60 density, 2-ply, 6.5 lbs/ft^2 with about a 1/4" crimp, fiberglass cloth, 7.5 oz. 16/14 "E"-glass; and (3) perforated aluminum foil for a radiation reflecting shield. Nextel has an operating temperature limit of 1200 C, and the "E"-glass has a limit of 425 C. Although this insulation design provided high permeability and reasonably good protection for the sheet, the knitted wire mesh was not sufficiently isolated and shorted to the heater near the end of the first field test. Furthermore, the ceramic cloth became brittle from the heating and thereafter was difficult to handle. The ceramic fibers also present an environmental hazard in large scale operations. More recent insulation designs using loose insulation, such as expanded vermiculite or perlite particles, avoid these difficulties. These materials are safe, non-toxic and highly effective for high temperature applications.

The flexible cover was a 20' x 20', fiberglass-reinforced, silicone-rubber sheet about 1/8" thick. A 2" diameter vacuum opening was located at the center of the sheet. This opening had a metal "stovepipe" fabricated into the sheet with fiberglass-reinforced, silicone-rubber sealant. The sheet was fabricated by Thorpe Inc., Houston, Texas. Twenty monitoring thermocouples, spaced about 2 feet apart, were attached to the upper side of the sheet with silicone adhesive. Since it is desirable to maintain the operating temperature sufficiently high to prevent condensation under the flexible sheet, yet below the allowable limit for silicone rubber (about 270 C), temperatures must be carefully monitored. An infra-red video camera was useful in detecting hot spots.

Power Supply and Data Acquisition System

The power supply and data acquisition system were integrated to provide automated process control and data collection. The heater was energized with a 300 amp, single-phase, 3-wire, 240/480 volt, 60 Hz, phase-angle-fired SCR power supply (Loyola EPAC-2-480-188). Underground power cables in PVC conduits conducted the power to a junction box, and then into the sand pit where they rose to the surface at the heater under the flexible sheet. Since SCR phase-angle-fired output is not a sine wave, power cannot be measured by simple averaging meters. Instead, RMS voltage, current, and power were measured with Ohio Semitronics transducers, (VT8-9B), (CTA-113), and (PC5-39-2B), respectively. The instruments were calibrated with two 150 KVA load simulators. Two Terra Technology PDL-100 data loggers were used to collect and store data from the power supply, and from 24 thermocouple locations. For safety, the thermocouple inputs were connected to the data logger through Analog Devices 2B50A optically isolated temperature transmitters. Thermocouples were buried in the soil, at the surface, and under the flexible sheet. Data was collected every minute.

Vacuum Collection System

The vacuum collection system was connected to the top of the flexible silicone-rubber sheet at the "stovepipe." See Figure 7. A heated vacuum line rose vertically about 8 feet and then ran nearly

horizontally 60 feet, where it entered the fluid collection system outside the test area at an elevation of 6 feet. The collection system consisted of a precooler and cyclone separator to remove the bulk of the liquids, a dry ice cold trap, vacuum pumps, an activated carbon trap, and an air flow meter. The vacuum in the soil was monitored by water manometers connected to buried tubing, with screened openings at depths of 0.5", 12", and 24", at locations near the center, the midpoint and the edge of the heater. A heated sampling line, which fed into the vacuum line upstream from the precooler, provided access for analyses in an analytical instrument truck, located adjacent to the fenced site.

Gasmer Field Experiment - GRUF #1 December 6-11, 1989

Following sampling of the hexadecane contaminated soil at the test site on November 28, 1989, the GRUF #1 heater blanket and sheet were placed on the sand. The average initial soil temperature was 19.2 C, and the average air temperature during the test was about 5 C.

1. *Vacuum Response*

A preliminary test of the vacuum system demonstrated that the vacuum pumps would vent about 16 cubic feet per minute with only a very small vacuum under the impermeable sheet (< 6" water manometer reading). Man-ometers connected by underground tubing in the soil beneath the heater showed nearly uniform vacuum down to a depth of 2 feet. See Figure 3. Attempts to increase the vacuum by improving the seal at the edge of the silicone sheet had little effect, partly because of wrinkles extending from the corners of the elevated heater blanket, and also because of the extremely high sand permeability (> 5 darcies). This high permeability allowed the air to enter the soil surface in the area outside the sheet and to flow readily into the test region.

Throughout the remainder of the heating test, the air flow rate was maintained at 16 CFM and all points in the sand under the sheet appeared to have a nearly common vacuum, equal to about 5 inches of water. Even at this small vacuum, the sheet appeared to have been pulled tightly to the soil except at the wrinkles. Conformance of the sheet with the soil surface improved during the several days of operation. Occasionally, however, the loose sand at the surface would shift and channels of flow would be observed under the sheet. A small amount of sand, placed at the edge of the sheet, temporarily prevented this channeling.

2. *Heating Rates and Temperature Response*

The heater was energized on December 6, 1989, at 15:34 hours. After about one hour (at 16:45) power was shut off in order to correct the flow of air around the central port and thereby minimize convective heating at the "stovepipe." This was accomplished by inserting a 3' x 3' stainless steel baffle sheet between the insulation layers directly under the central port. On December 7, 1989, at 11:05 hours, the heater was again energized and the main test was begun. Initially, about 40 KW of electrical power (190 VAC and 210 Amps) was used. At 400 watts/ft^2 of heated area, the temperature at the surface of the sand under the heater rose to 300 C in about 10 hours and to 375 C after 22 hours. At that time (December 8, 1989, 9:01 hours) the power was increased to about 55 KW (280 VAC and 200 Amps). During this period, surface soil temperatures reached 575 C at the center of the pattern, and the difference in temperature across the insulation layer was about 300 C. After almost two days at 55 KW rate, the heater failed on December 10, 1989, at 4:24 hours. The vacuum pumps were immediately shut down to minimize recontamination of the soil near the surface by vaporized contaminants from the deeper, partially-heated soil. Twelve hours after the power loss, the surface temperature at the center of the pattern had fallen from 575 C to 250 C; after 30 hours the temperature had fallen to 135 C. At that time (December 11, 1989, 08:45) the data acquisition was terminated, and the sheet and insulation were removed and inspected.

During the heating periods, temperatures were measured with thermocouples buried at fixed locations under the center, middle, and edge of the heater. The center temperatures at several depths in the soil are shown in Figure 8. Initial soil temperature rise, as a function of heating rate, distance and time were compared with the constant flux solution given by Carslaw and Jaeger.[7] See Figure 9. Using estimated thermal properties of dry and water saturated sand, calculated temperatures at the surface were compared with the observed temperatures for conditions at the Gasmer test site. See Figure 10. The rate of rise in

temperature at the soil surface is well below the calculated values. Large surface heat losses from the hot flexible sheet is the major source of this reduced rate. It is estimated that only about half of the output of the heater was conducted downward into the soil. Other reasons for the slower temperature rise are the vaporization of water and the counter-current flow of vapors and air. If heat fluxes are corrected for surface heat losses, the temperatures at each measured depth rose initially as expected for a partially water-saturated sand. Upon approaching 100 C, however, the temperature remained nearly constant until all of the water was vaporized. Thereafter, the temperature again rose. The maximum temperatures that were attained at various depths in the soil at the center of the 10' x 10' pattern are shown in Table 1.

Because of the limited size of the heater, and the premature termination of the test, only part of the contaminated volume (10' x 10' x 1.5') reached temperatures needed for complete removal. A travelling thermocouple inside a conduit buried one foot under the heater quantified the extent of the greater heat losses at the edge of the pattern. After power-off, temperature fall-off in the subsurface was slower than at the surface. In fact, subsurface temperatures continued to rise after the power loss. At a depth of 12" at the center of the pattern, temperature rose from 167 C to 195 C, 10 hrs. after the power loss, and, thereafter, fell to 175 C after one day. At 18" depth, the temperature rise persisted for about 28 hrs.

3. ***Production Response***

Production collection facilities, described previously, allowed precise measurement of condensed water from the vacuum stream, and an approximate measurement of the noncondensable gas stream, which was almost all air. Only a small amount of liquid or solid hexadecane was observed in the large volume of water that was collected at the separators. The total amount of hexadecane, including solids in the cold traps, is estimated to be less than 50 grams. Alternatively, total hydrocarbon analyses (by a Ratfisch Flame Ionization Detector) of the vapor sample stream provided a good estimate of the upper limit of hexadecane produced. Since most of the hexadecane in this stream had been oxidized, CO_2 analysis provided the majority of closure for the material balance of the total hexadecane removed. See Appendix A. Other organic compounds that were originally present in the river sand are also detected by these in-line analyses; however, comparison of these values with before/after soil samples reveal that the "other organic compounds" are only about 5.5% of the total. A summary of total fluid production is given in Table 2.

Air was produced at a constant rate of 16 SCF/min for a total of 63 MCF in the 65.3 hours of heating. A malfunction of the first flow meter and low precision of the replacement meter introduced the substantial uncertainty in cumulative air produced.

Water production commenced about two hours after the start of heating at an initial rate of 3 gal/hour. The rate declined throughout the test, but water was still being produced at a rate of about one gal/hr at the end of heating. See Figure 11. Most of the water was collected at the cyclone separator, and less than 2% of the total 128 gallons recovered was found in the downstream dry ice trap. Most of the carry-over to the dry ice trap resulted from operational problems early in the experiment. When air temperatures were below 20 C, small amounts of solid hexadecane were observed on the surface of the produced water but a quantitative estimate from produced samples was not feasible.

4. ***Post-Experiment Observations***

Following termination of the experiment, the heater blanket was removed about 30 hours after power-off and the soil surface was inspected. The Brazos River sand had been oxidized from a buff color to a darker red-orange and extensive "dry-mud" polygonal patterns of shallow vertical cracks were found throughout the heated area. High temperatures extended only a few inches beyond the edge of the heater.

Post-heating sample holes were taken on December 11, 1989, from 11:30-16:30 hours. Results of analyses for residual hexadecane are tabulated in Tables 3 and 4. Contours of residual hexadecane on a north/south cross-section through the center of the heated pattern in Figure 12 may be compared with maximum temperature isotherms from the fixed thermocouples on one-half of the east/west cross section in Figure 13. This comparison shows that the temperature exceeded the normal boiling point of hexadecane (287.5 C) down to about 6" and that removal of hexadecane was highly efficient in that region (residual about 0.5 mg/kg). Temperatures exceeded the boiling point of water down to about 18 inches. At that temperature only about 75% of the contaminant was removed. Because the experiment ended before adequate heating at that depth, and because the vacuum pumps were shut down to avoid resaturating the upper levels, some

of the hexadecane was driven down below the 18-inch level. Note that warming at this depth continued for more than 28 hours after vacuum shut-down. Transport of contaminant to a greater depth could have resulted from both condensation and vapor phase diffusion in this partially liquid-saturated region. Only a very small amount of lateral spreading of hexadecane was observed in soil samples outside the 10' x 10' test area. See table 4. From the initial contamination of 812 ppm hexadecane, about 85% was removed by the surface blanket heating. Table 5 shows the average removal of hexadecane as a function of depth in the contaminated zone.

The overall material balance of *in-situ* and produced fluid components are given in Appendix A and the resultant heat balance is given in Appendix B.

RESULTS AND CONCLUSIONS

The vacuum-assisted surface heating method for removal of shallow soil contaminants was successfully demonstrated under field conditions with a 10' x 10' heating blanket. Observations on process behavior and equipment performance, from this experiment (GRUF #1), and from subsequent experiments, have provided experience needed to develop commercial applications for this soil remediation method. These observations are summarized below:

Process Behavior

1) A vacuum can be applied to the soil under a ground-conforming, impermeable sheet on the surface. The vacuum contained the volatilized products under the sheet and allowed collection into a closed system. Only a small vacuum (less than 6" of water) could be attained in this high permeability, water-saturated sand, but the vacuum was nearly uniform in the soil down to a depth of 2 feet.

2) A bare wire electrical heater, placed directly on a soil surface, safely transferred energy into the soil. Electrical potentials in the ground outside the sheet were very low (less than 100 millivolts).

3) The phase-angle-fired SCR power supply and monitoring instruments provided excellent operational control during the experiment and allowed accurate measurement of the power input to the heater. An average of about 500 watts/sq ft electrical power was applied at the soil surface over a period of 2 1/2 days; however, of the total 11 MM BTUs of heat generated, less than half was conducted downward into the soil.

4) Maximum soil temperatures reached 576 C at the surface, 345 C at a depth of 6", 195 C at 12", and 102 C at 18".

5) A total of 63 MCF air was produced into the vacuum system and vented to the atmosphere. This was over thirty times the amount of air needed to completely oxidize the hexadecane.

6) A total of 21.3 MCF of water was vaporized in the soil and condensed to 128 gallons in the liquid collection traps.

7) Only a small amount of hexadecane (<50 grams) that was removed from the soil was captured in the liquid/dry ice traps. Most of the produced hexadecane stream had been oxidized to CO_2.

8) Of the total 812 ppm hexadecane initially in place, the process removed 99.94% in the first 6" of depth, leaving only 0.5 ppm residual. Although heating was interrupted by a heater failure, substantial removal by steam distillation occurred at greater depths. Thus, even though maximum temperatures were well below the boiling point of hexadecane, 98% was recovered from 6" to 12", and 75% from 12" to 18".

9) Some hexadecane was driven down below the original 18" contamination layer because of the intentional shut-down of the vacuum pump after heater failure and before the soil had cooled. This was done to prevent resaturation of the shallow regions. There was little evidence of lateral spreading beyond the heated area.

10) Heating rate in the soil was slower than calculated for simple thermal conduction because of: a) excessive heat losses from the surface of the sheet, b) high water content of the sand, which required additional energy for vaporization, and c) large upward convection of vapors and air.

Advantages of the Method

Advantages of the surface heating blanket method for soil remediation are:

1) Costs are lower than those for removal of the soil or for excavation and on-site incineration.

2) The soil is not disturbed; secondary contamination during remediation is avoided.

3) Large scale transport of hazardous wastes is avoided.

4) The vacuum imposed on the test site provides containment of contaminants underground and easy collection of produced materials into a closed system.

5) The process decomposes a majority of the contaminants in-place before they are produced, and thereby avoids surface incineration or other disposal.

6) Very low levels of contaminant are attained in soils where temperatures exceed the boiling point of the contaminant..

FUTURE R&D

More durable heaters and improved surface insulation blankets have been designed and tested; however, scale up to some commercial operations will require the use of heater blankets as large as 2000 square feet. For such applications, new operational and facilities concepts are needed for practical movement of the equipment and logistics of the heating/cooling cycle operations. In addition, the development of an in-line thermal oxidizer to remove the final amounts of contaminants from the product stream could eliminate the need for liquid traps, and allow the vacuum system to be maintained above the dew point, thereby permitting the water vapor to be vented to the atmosphere.

ACKNOWLEDGEMENTS

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APPENDIX A - OVERALL MATERIAL BALANCES

Hexadecane

An overall material balance of the hexadecane contaminant is shown in Table A-1. The amount of hexadecane initially mixed into the sand (1) was measured gravimetrically. Hexadecane in soil samples before heating (2), and after heating (3), were first extracted by a hexane/acetone wash and then analyzed by flame ionization detection (FID); hexadecane in the produced stream (5a) was obtained from FID of a small side stream. CO_2 in the produced stream (5b) was also obtained from a detector in the side stream.

Calculated value of initial hexadecane weight from FID of soil samples taken at the time of packing (2) agreed within 1% of the initial gravimetric weight (1). This difference shows that very little, if any, additional organic material was extracted from the soil by the solvent wash.

The calculated hexadecane from the sum of the produced stream products plus the amount remaining from soil samples after heating, (5a +5b +3) exceeds the initial weight by 5.8%. The excess probably results from additional soil pyrolysis and oxidation products in the produced stream. The source of such compounds is the carbonaceous debris and other organic materials that are found in river sands. An analysis of products from pyrolysis of the sand without hexadecane, which would have verified the level of these organic compounds, was not obtained. Fortunately, the amount of these compounds is relatively small and the measurement of hexadecane remaining in the soil after heating (3) is affected, at most, by the even smaller amount (about 1%) of solvent-soluble organics in the soil .

Produced Air Volume

Based on the bulk volume of the 10' x 10' x 1.5' contaminated soil, and 43% porosity, the pore volumes of air convected through this region are:

$$\frac{63{,}000}{(10 \times 10 \times 1.5)\,(0.43)} = 976 \text{ pore volumes}$$

Produced Water Volume

The volume of water produced, compared to the volume of pore space in the contaminated region, is:

$$S_w = \frac{(128 \text{ gals})}{(7.48 \text{ gal/cu.ft.})} \times \frac{1}{(10 \times 10 \times 1.5 \times 0.43)} = 0.265$$

Thus, if all of the water came from the contaminated region, it would represent a saturation of 26.5% of the pore space of the contaminated region, or about 7.6% by weight of the soil. This calculated water saturation appears to be higher than expected for a 5 darcy sand, and it appears likely that some rainwater was pulled into the heated region from the sides and the bottom during the test.

APPENDIX B - OVERALL HEAT BALANCE

The overall heat balance is displayed in Table B-1. The total heat injected is calculated, assuming 40,000 watts for 22 hours and 55,000 watts for 43.3 hours. Produced heat is based on, (a) a constant flow of air at 16 SCF/min, which was heated to the average surface heater temperature of 425 C, and a specific heat of air equal to 0.25 BTU/#-^{o}F, and (b) 128 gal. of produced water, superheated to 425 C, requiring 1400 BTU/#H_2O. All temperatures were measured in Celsius units; however, most other field equipment, measurements, and heat transfer correlation's are in customary English units. For this reason English units

are used in heat loss and heat balance computations, and Celsius units will be used, but converted in place in the equations.

Surface Heat Losses

Surface heat losses to the air above the blanket are based on the equation of McAdams, corrected by a wind factor, f. The average temperature of the upper surface of the heater blanket was 155 C. The estimated weather conditions during the test are as follows: (a) average ambient air temperature = 5 C, (b) average wind velocity 10 mph, and (d) cumulative rainfall during the test = approximately 0.2".

$f = 1 + 0.1627\ v_A - 0.0058\ (v_A)^2 + 0.0000933\ (v_A)^3$

v_A = wind velocity (mph)

$f = 2.14$

T = average temperature difference (C) = 150 C

$h = 0.38 \times (1.8 \times T)^{0.25}$ [BTU/hr-ft^2- F]

$h = 0.38 \times (1.8 \times 150)^{0.25} = 1.54$ BTU/hr-ft^{2-o}F

The total heat loss, Q_L (BTU), at the upper surface is:

$Q_L = (h) \times (f) \times (A) \times (1.8 \times T) \times (t)$

A = area (ft^2) = 100 ft^2

t = time (hours)

$Q_L = (1.54) \times (2.14) \times (100) \times (1.8 \times 150) \times (65.3)$

$= 5.8$ MM BTU

Heat required to boil off the rainwater was (10 x 10 x 0.2/12)(62.4)(1150-9) 0.1MM BTU. Therefore the estimated total heat loss from the upper surface is 5.9MM BTU.

Heat Remaining in Soil at End of Test

The heat remaining in soil at the end of heating, above the initial soil temperature (T_o = 19.2 C), is calculated from average temperatures measured in four layers of equal thickness, (L = 0.5 ft). The temperatures represent depths as follows: T_1, from 0 to 0.5 ft; T_2, from 0.5 to 1 ft; T_3, from 1 to 1.5 ft; and T_4, from 1.5 to 2 ft. Although not measured, the extrapolated average temperature T_5, from 2 to 3 ft, is about 50 C and almost unchanged below that. The volumetric specific heat of the soil is estimated to be: M = 30 BTU/cu.ft.- F. Therefore, the heat remaining (Q_s) is:

$Q_s = (M)x(A)x[\ L(1.8)(T_1-T_o + T_2-T_o + T_3-T_o + T_4-T_o +$
$T_5-T_o)]$

$Q_s = (30)x(100)x[0.5(1.8)(430-19.2 + 250-19.2 + 140-$
$19.2 + 90-19.2)] + (30)x(100)x(1.0)(1.8)(50-19.2)_{est.}$

$Q_s = 2.25 + 0.18_{est.} = 2.43$ MM BTU

The overall heat balance shown in Table B-1 accounts for nearly all of the injected, produced, and remaining heat in the process; however, there is a large uncertainty in heat losses from the heater blanket surface.

SI METRIC CONVERSION FACTORS

BTU	x 1.055056	E+00 = kJ

BTU/#-^{o}F	x 4.1868	E+00	= kJ/kg K
BTU/hr-ft^{2-o}F	x 5.678263	E-03	= kW/m^{2} K
BTU/hr-ft-^{o}F	x 1.730735	E+00	= W/m K
CFM, cuft/min	x 4.719474	E-04	= m^{3}/s
Darcy	x 9.869233	E-01	= μm^{2}
degree F	[(^{o}F-32)/1.8]		= C
feet	x 3.048	E-01	= m
gal	x 3.785412	E-03	= m^{3}
gal/hr	x 1.051503	E-03	= dm^{3}/s
inches	x 2.54	E+01	= mm
inches $H_2O_{at\ 60\ ^{o}F}$	x 2.4884	E-01	= kPa
MCF	x 2.831685	E+01	= m^{3}
mesh	x 3.937	E+01	= openings/m
mph	x 1.609344	E+00	= km/hr
ppm	x 1.0*	E+00	= mg/kg
watts/ft^{2}	x 1.07639	E+01	= W/m^{2}

Table 1

MAXIMUM SOIL TEMPERATURES
After 65.3 Hours of Heating
Center of Pattern

Depth	*Maximum Temperature (°C)*
0	575
6"	345
12"	195
18"	102
24"	91

Table 2

TOTAL PRODUCED FLUIDS

Air	63 MCF	= 5089# ± 10%
Water	128 gal = 21.3 MCF	= 1066# ± 1%
Hexadecane + Soil Organics		
From THC Analyses	356 gm	
From CO_2 Analyses	4269 gm	
Total	4625 gm	= 10.2# ± <1%

Table 3

HEXADECANE CONTENT BEFORE HEATING
Soil Samples Taken at Three-Inch Depth Intervals

Sample Location (ft)*		*Hexadecane Concentration (mg/kg)*						
x (East)	y (North)	0-3"	3"-6"	6"-9"	9"-12"	12"-15"	15"-18"	>18"
1	1	760	885	890	760	790	840	0
1	9	700	940	810	770	800	850	0
3	3	810	820	890	785	790	880	0
3	7	690	860	800	820	790	770	0
5	1	790	910	860	780	800	860	0
5	3	790	890	850	820	820	800	0
5	4	790	870	810	820	830	750	0
5	5	660	870	810	730	860	800	0
5	6	710	880	840	800	800	825	0
5	7	780	915	790	850	820	900	0
5	9	640	860	830	810	800	740	0
7	3	780	850	880	830	820	750	0
7	7	680	890	860	750	840	800	0
9	1	780	850	840	860	830	890	0
9	9	710	760	820	860	780	760	0

*Coordinates are from the origin (0,0) at the southwest corner of the heater.

Table 4

HEXADECANE CONTENT AFTER HEATING Soil Samples Taken at Six-Inch Intervals						
Sample Location* (ft)		Hexadecane Concentration (mg/kg)				
x (East)	y (North)	0-6"	6"-12"	12"-18"	18"-24"	24"-30"
1	1	0.43	37	238	123	50
1	9	0.8	39	174	577	50
3	3	0.09	2.4	78	42	59
3	7	0.53	2.9	85	215	27
5	1	0.50	4.4	442	58	57
5	3	0.09	2.9	99	116	39
5	4	0.074	12	49	80	27
5	5	0.16	5.1	25	148	41
5	6	0.17	23	174	193	46
5	7	0.47	1.2	224	23	28
5	9	0.4	2.3	494	105	14
7	3	0.5	1.7	86	101	58
7	7	1.6	1.7	88	179	81
9	1	0.07	64	220	41	32
9	9	-	-	-	-	-
-1	5	0.15	0	0	0	0
5	-1	0.99	0	0	0	0
5	11	0.15	0	0	0	0
11	5	0.25	0	0	0	0

- Coordinates are from the origin (0,0) at the southwest corner of the heater.

Table 5

REMOVAL OF HEXADECANE FROM CONTAMINATED ZONE AS A FUNCTION OF DEPTH		
Depth of Layer	Average Residual n-$C_{16}H_{34}$* (ppm)	% Removal
0-6"	0.42	99.94
6"-12"	14.26	98.0
12"-18"	176.86	74.7

*Includes about 1% other organic compounds soluble in hexane/acetone.

Table A-1

OVERALL HEXADECANE MATERIAL BALANCE Gasmer Experiment GRUF #1		
	Weight (gms)	Percent of Original Hexadecane
INITIAL BEFORE HEATING		
1) Weight $C_{16}H_{34}$ originally added to sand	5130	100%
2) Calculated $C_{16}H_{34}$ + soluble soil organics from analysis of 90 soil samples taken before heating (15 locations x 6 layers)	5177	100.9%
RESIDUAL AFTER HEATING		
3) Calculated $C_{16}H_{34}$ + soluble soil organics from analyses of 90 samples taken after heating (18 locations x 5 layers)	803	15.7%
QUANTITY REMOVED		
4) Calculated from soil sampling [(2)-(3)]	4374	85.2%
5) Calculated from production sampling		
a) $C_{16}H_{34}$ + soil organics' pyrolysis products obtained from THC analysis	356	
b) $C_{16}H_{34}$ + soil organics' oxidation product from CO_2 analysis	4269	
c) Total C16H34 + soil organics [(5a)+(5b)]	4625	90.2%
d) Approximate soil organics [(5c)+(3)-(1)]	298	5.8%
ORIGINAL TOTAL ORGANICS		
From Production Samples + Residual Samples [(5c)+(3)]	5428	105.8%

Table B-1

HEAT BALANCE Gasmer Experiment (GRUF #1)		
	MM BTU	Percent of Total Injected Heat
PRODUCED & SOIL HEAT		
Produced Heat:		
Convected Air 63 MCF	0.95 ± 0.2	8.5
Steam Vapor 128 gal, @ 425°C	1.50 ± 0.1	14
Surface Loss (est.)	5.90 ± 0.5	53
Heat Left in Sand		
In upper 2 ft	2.25 ± 0.1	20
Below 2 ft	0.18	1.5
TOTAL PROD. + SOIL HEAT	10.78	97
INJECTED HEAT	- 11.1	100
DIFFERENCE	- 0.32	3

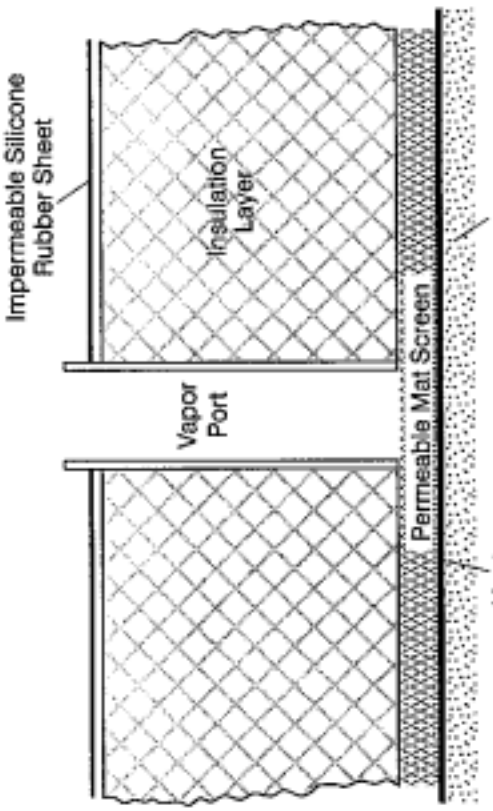

Figure 2 – Cross Section of Heater Blanket.

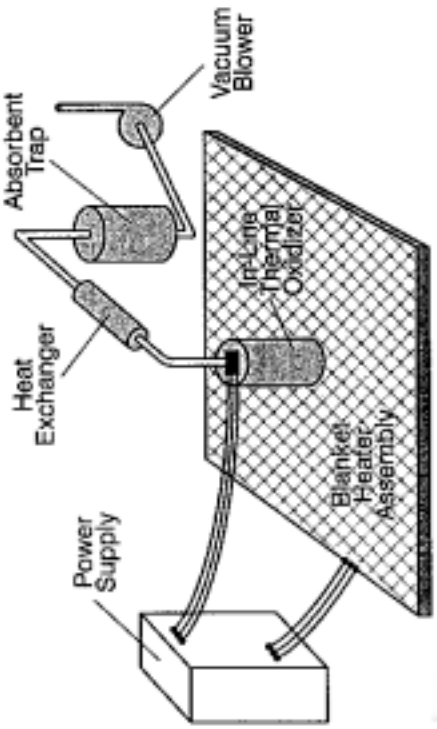

Figure 1 – Surface Heating and Vacuum Extraction Facility.

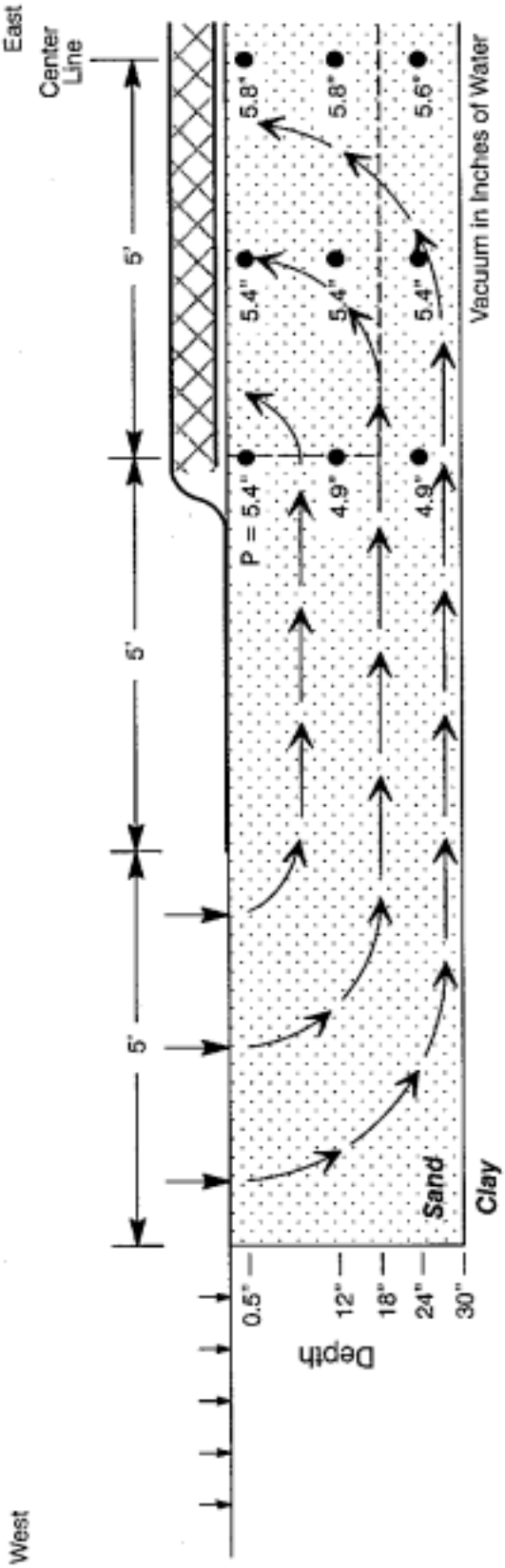

Figure 3 – Air Flow Patterns and Subsurface Soil Vacuum

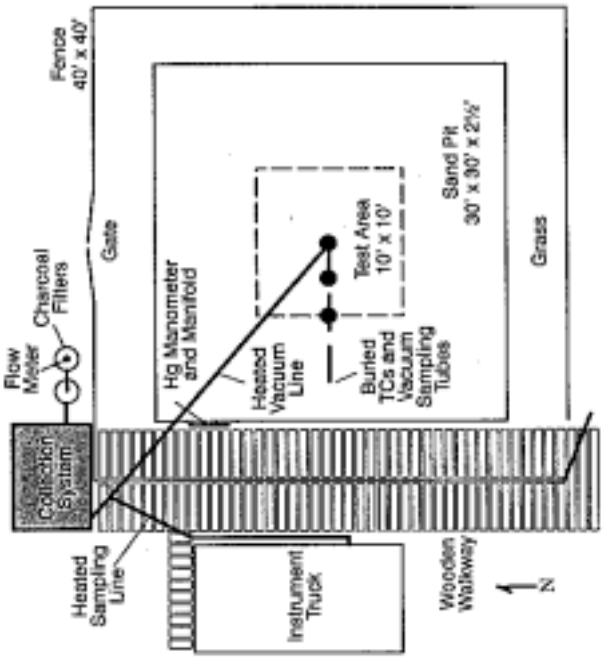

Figure 6 – Plan View of Gasmer Road Soil Remediation Site.

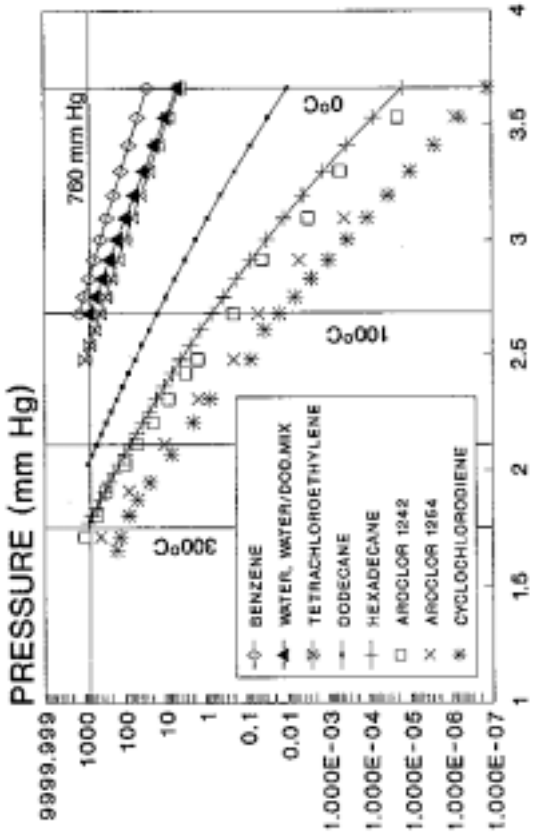

Figure 4 – Vapor Pressure of Contaminants.

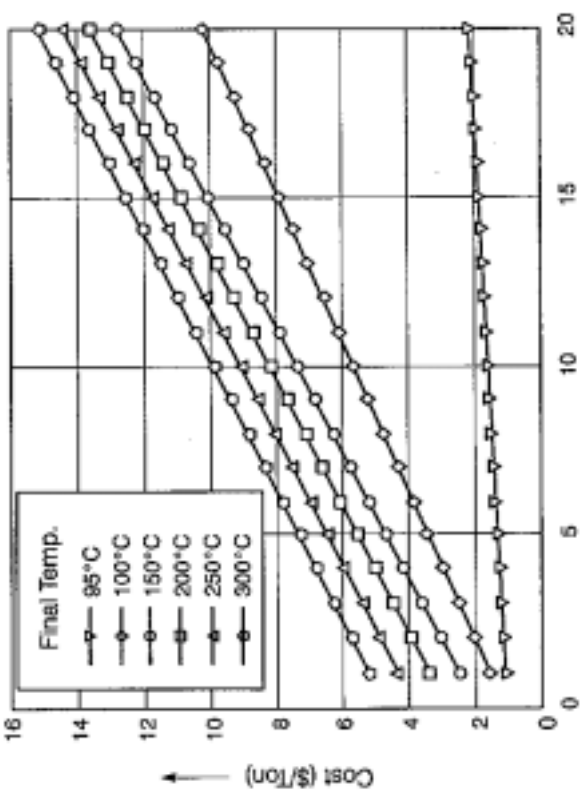

Figure 5 – Electrical Cost of Heating Moist Soil.

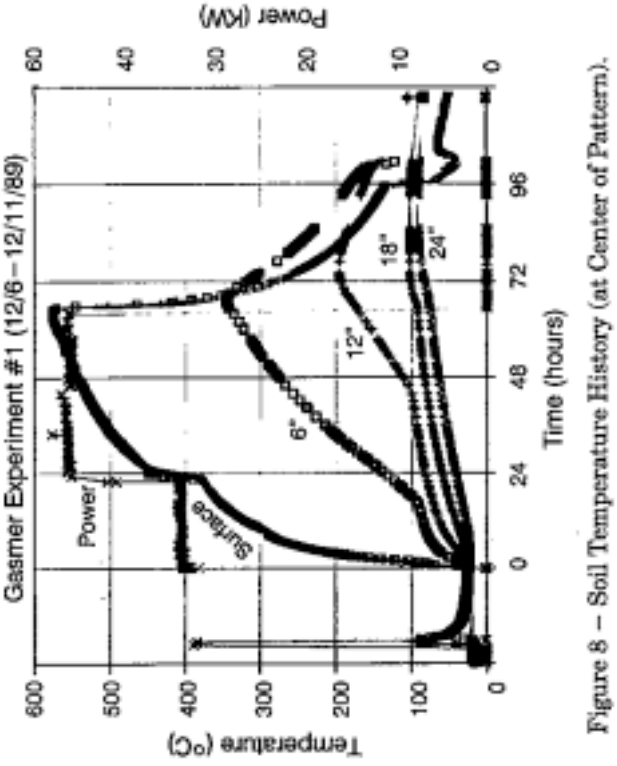

Figure 8 – Soil Temperature History (at Center of Pattern).

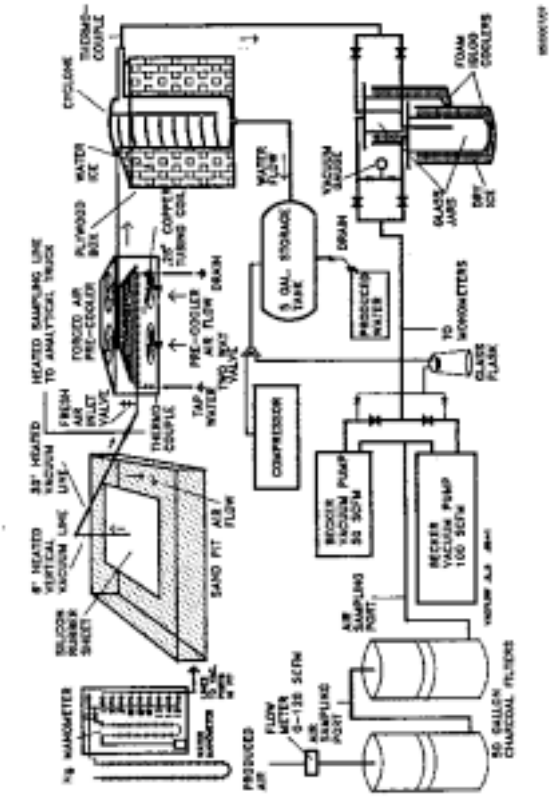

Figure 7 – Vacuum Collection System.

Soil Surface Heating Temperature Rise (ΔT)
at Depth (x) time (t)

$$\Delta T(x,t) = \frac{2F_o}{\lambda}\left\{\left(\frac{\alpha t}{\pi}\right)^{1/2} e^{-x^2/4\alpha t} - \frac{x}{2}\left[1 - \frac{2}{\sqrt{\pi}} e^{-x^2/\alpha t} \sum_{k=0}^{\infty} \frac{2^k\left(\frac{x}{2\sqrt{\alpha t}}\right)^{2k+1}}{(2k+1)!!}\right]\right\}$$

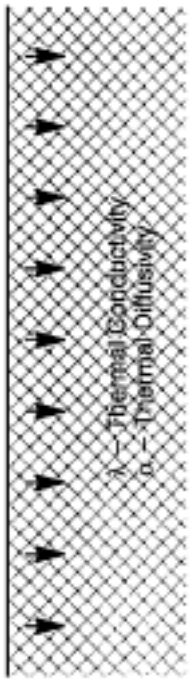

Figure 9 – Constant Flux Heating from a Plan Surface.

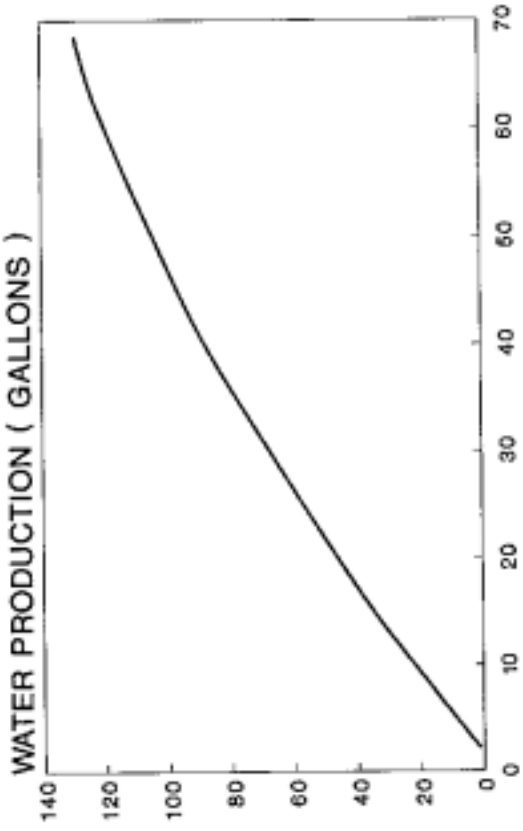

Figure 11 – Cumulative Water Production.

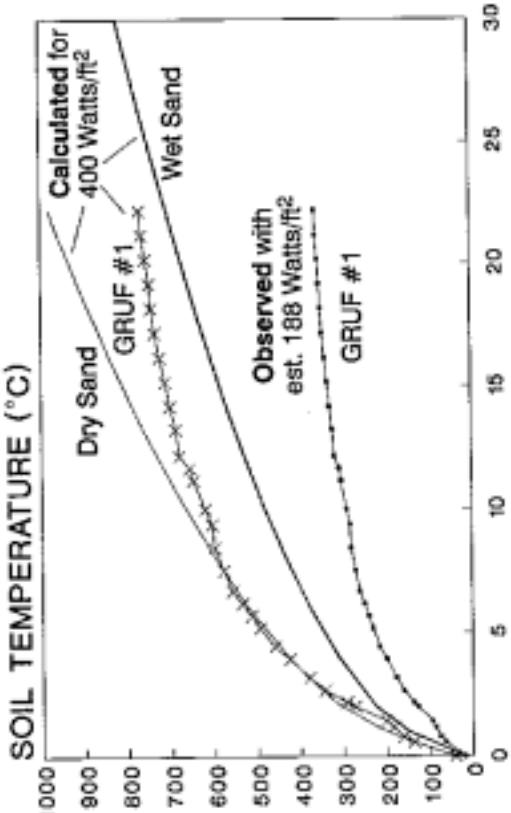

Figure 10 – Calculated Initial Temperature Rise at the Surface Compared to Field Experimental Results.

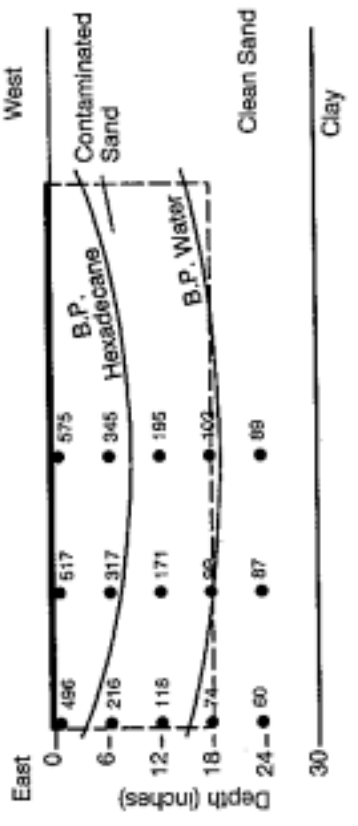

Figure 13 – Highest Temperature in Soil (°C) during Experiment (E-W Vertical Section at Middle of Heater).

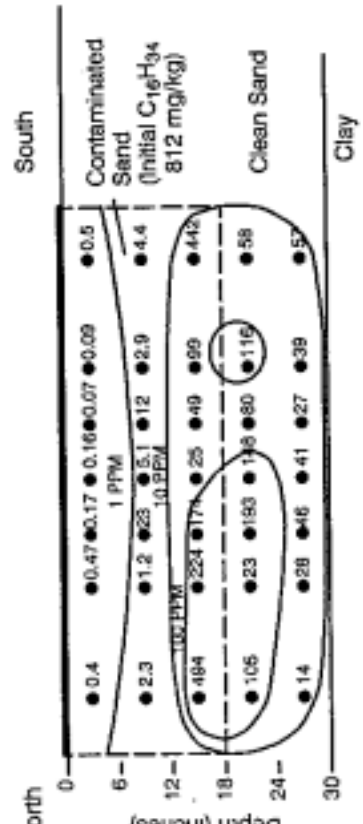

Figure 12 – Residual Hexadecane in Soil (mg/kg) after Heating (N-S Vertical Section at Middle of Heater).