

Removal of volatile organic compounds from soil

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Abstract

Pollution by petroleum products is a source of volatile organic compounds in soil. Therefore, laboratory column venting experiments were completed in order to investigate the removal of a pure compound (toluene) and a mixture of two (toluene and n-heptane) and five (toluene, n-heptane, ethylbenzene, m-xylene and p-xylene) compounds. The choice of the compounds, as well as their proportion in the mixture, was made on the basis of the real fuel composition. The objective of this study is a comparison between the experimental volatile organic compounds removal results and the computational fluid dynamics (CFDs) analysis. The proposed model for the contaminants transport describes the removal of organic compounds from soil, the contaminants being distributed among four phases: vapor, nonaqueous liquid phase, aqueous and “solid”; the local phase’s equilibrium and the ideal behavior of all four phases was found to be accurate enough to describe the interphase mass transfer. The process developed in the lab consists of a heater/boiler that pumps and circulates hot oil through a pipeline that is enclosed in a larger-diameter pipe. This extraction pipe is vertically installed within the contaminated soil up to a certain depth and is welded at the bottom and capped at the top. The number of heat source pipes and extraction wells depends on the type of soil, the type of pollutants, and the moisture content of the soil and the size of the area to be cleaned. The heat source heats the soil, which is transported in the interior part of the soil by means of conduction and convection. This heating of the soil results in vaporization of the gases, which are then driven out of the soil by the extraction well. The extraction well consists of the blower, which sucks the vaporized gases out of the system. Our previous studies have removed higher boiling compounds, such as naphthalene, etc., to a non-detectable level. Thus, the current technology is very promising for removing most of the chemical compounds; and can also remove these high boiling compounds from the saturated zone. The reasonable



agreement between the predicted and the experimental results as well as the values of the performance criteria prove that the mathematical model is suitable to describe the removal of volatile organic compound pollutants by venting in the range of experimental conditions used in the pilot plant.

Keywords: soil remediation, vapor extraction, volatile organic compound removal.

1 Introduction

With environmental safety being of prime importance, the remediation systems for cleaning soil of polluting chemicals have gained importance in recent years. Different remediation processes, such as venting [3] for soil contaminants like diesel, the solvent washing of soil [4] for contaminants like pentachlorophenol (PCP), which is a wood preserving agent, have been studied and used for this purpose. Soil vapor extraction (SVE) has been used at many sites to remove volatile organic compounds (VOCs) from soil in the vadose zone. The effectiveness of SVE, however, is limited at sites with complex geology or by the distribution of contaminants in the subsurface and saturated soils. In recent years, research and field demonstrations have been conducted using innovative technologies and procedures to enhance the treatment effectiveness and removal rates of VOCs from vadose zone soil and of VOCs dissolved in groundwater and adsorbed to saturation zone soils. Various pollutants, such as fuels and other chemicals leaking into soil, pose a high environmental threat. The research analysis focuses on heated soil vapor extraction with air sparging, which is a remediation process primarily used to clean the soil of pollutants, such as organic compounds that include solvents, fuels and para nuclear aromatics (PNAs). Figure 1 shows the schematic sketch of this process [2].

The system consists of heating and suction wells embedded into the soil. The heating pipes are connected to the main pipeline, which is connected to the boiler

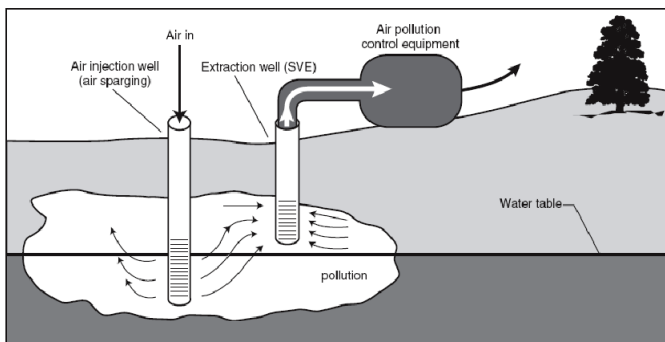


Figure 1: Schematic of a HSVE and air sparging system [2].

and re-circulating pump. Through this heating pipe heated oil at approximately 500°F is supplied to the heating wells. Heat is diffused out of the heating well into the soil and vaporizes the contaminants. These contaminants are removed from the soil by the suction well, which is connected to a storage tank where the contaminants are stored for temporary purposes. Finally the contaminants are disposed of from time to time as air is blown through the air-sparging well to drive out the contaminants from the saturated zone to the unsaturated zone.

Previous research work on this process [5-7] has proved the feasibility and effectiveness of the process. Application of this process in real-life cases has shown that, in soil contaminated with volatile organic compounds (VOCs), the contaminant concentrations can be brought down to non-detectable levels or below acceptable government standards.

A two-month experiment study was conducted to demonstrate the effectiveness in degradation of hydrocarbons and to remove volatile constituents in the saturated soil. The soil samples (approximately 15 lbs) were obtained from two different depths at 10 feet (saturated) that represent typically contaminated MGP soil without light nonaqueous-phase liquid (LNAPL) or dense nonaqueous-phase liquid (DNPL) layers.

Laboratory experiments were conducted at the University of Wisconsin-Milwaukee. Soil placed in the experimental setup was subjected to a heat of about 125°F and a vacuum of nearly 13in-Hg. These values were chosen in order to simulate actual conditions. The samples have been periodically analyzed for VOCs and PAHs using Soxhlet extraction and Gas Chromatography (GC). (See below)

2 Experimental set-up

The experimental setup is constructed to simulate the actual conditions in the closest possible way. It consists of two round bottom (RB) flasks, a super condenser, carbon cells, and vacuum pump. A picture is shown in Figure 2.

The larger of the two round bottom flask contains the soil and is heated from the bottom by a heating mantle. A thermo couple is inserted to monitor the temperature. An air spurge is also provided. An air flow meter is used to control the amount of airflow and is kept at 50cc/min. The air and gases (from the soil) at the beginning of the flow path are led through a super condenser, cooled by tap water, to a smaller RB flask receiver, which is placed in coolant (dry ice), the flow path continues through activated carbon cells, to the vacuum pump. This elaborate procedure ensures that there are no gases escaping to the atmosphere.

Cold tap water and not coolant is used in the condenser to avoid the situation of freezing the water vapor from the soil in the condenser and clogging the flow path. The smaller flask in the dry ice bath acts as collecting flask and collects the condensed liquid. Due to the air spurge, the flow velocities of the gases are high and thus the condensation in both the condenser and the trap would not be very effective. Hence, the carbon cells have been used to further trap any remaining vapors from the soil.



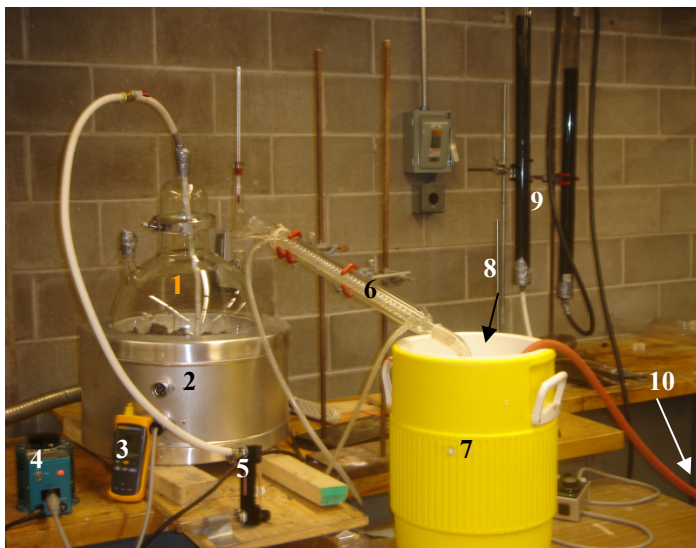


Figure 2: Experiment set up. 1. Flask and soil. 2. Heating mantle. 3. Thermometer. 4. Heat controller (Variac). 5. Airflow meter. 6. Super-condenser. 7. Coolant. 8. Receiver flask. 9. Activated carbon cells (2 nos.) 10. Vacuum pump (not showing).

2.1 Running of the experiment

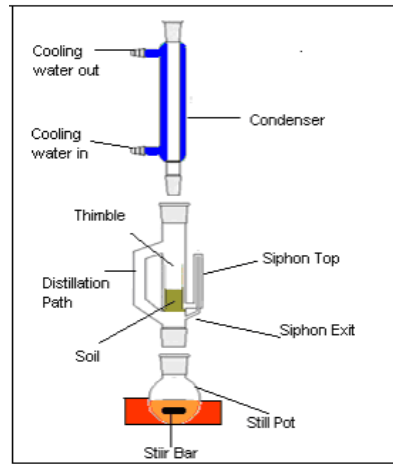
Saturated soil was heated for 600 hours real time (25 days) with a constant temperature of 125°F, airflow of 50cc/min and a vacuum of 13in-Hg. The soil was tested for remaining compounds at 3, 19, and 25 days of heating. A ¼ lbs sample of treated soil was randomly sampled at each interval and Soxhlet extraction was performed for 24hrs using 200ml of dichloromethane (CH_2Cl_2) as solvent. The solvent dissolves, extracts and concentrates the compounds (VOCs) in the soil and the GC-MS is performed to separate and analyze the compounds in the concentrated solvent.

2.2 Soxhlet extraction

The Soxhlet extractor is a piece of laboratory apparatus invented in 1879 by Franz von Soxhlet [9]. It was originally designed for the extraction of a lipid from a solid material.

The contaminated soil is placed inside a “thimble” made from thick filter paper, which is loaded into the main chamber of the Soxhlet extractor. The Soxhlet extractor is placed onto a flask containing the extraction solvent. The Soxhlet is then equipped with a condenser.

The solvent is heated to reflux by heating mantle. The solvent vapor travels up a distillation arm, and floods into the chamber housing the thimble of solid. The condenser ensures that any solvent vapor cools and drips back down into the chamber housing the soil.



(a) Picture of Soxhlet extraction (b) Schematic sketch of Soxhlet extraction

Figure 3: Soxhlet extraction [9].

The chamber containing the soil slowly fills with solvent. Some of the desired compound will then dissolve in the solvent. When the Soxhlet chamber is almost full, the chamber is automatically emptied by a siphon side arm, with the solvent running back down to the distillation flask. This cycle may be allowed to repeat many times, over hours or days; in this study it was repeated for 24hrs.

During each cycle, a portion of the non-volatile compound dissolves in the redistilled solvent. After many cycles the desired compound is concentrated in the distillation flask. To illustrate this apparatus a picture and schematic sketch have been placed in Figure 3(a) and 3(b), respectively.

2.3 Gas chromatography

The GC is a type of chromatography [9] in which the mobile phase is a carrier gas, usually an inert gas such as helium, nitrogen or hydrogen and the stationary phase is a microscopic layer of liquid or polymer on an inert solid support, inside glass or metal tubing, called a column. The instrument to perform gas chromatographic separations is called a gas chromatograph. A gas chromatograph is a chemical analysis instrument for separating chemicals in a

complex sample. The gas chromatograph uses a flow-through narrow tube known as the column, through which different chemical constituents of a sample pass in a gas stream (carrier gas, mobile phase) at different rates depending on their various chemical and physical properties and their interaction with a specific column filling, called the stationary phase. As the chemicals exit the end of the column, they are detected and identified electronically. The function of the stationary phase in the column is to separate different components, causing each one to exit the column at a different time (retention time). Other parameters that can be used to alter the order or time of retention are the carrier gas flow rate, and the temperature.

In a GC analysis, a known volume of gaseous or liquid analyte (a substance or chemical constituent that is determined in an analytical procedure) is injected into the "entrance" (head) of the column, usually using a micro-syringe (or, solid phase micro-extraction fibers, or a gas source switching system). Although the carrier gas sweeps the analyte molecules through the column, this motion is inhibited by the adsorption of the analyte molecules either onto the column walls or onto packing materials in the column.

The rate at which the molecules progress along the column depends on the strength of adsorption, which in turn depends on the type of molecule and on the stationary phase materials. Since each type of molecule has a different rate of progression, the various components of the analyte mixture are separated as they progress along the column and reach the end of the column at different times (retention time). A detector is used to monitor the outlet stream from the column; thus, the time at which each component reaches the outlet and the amount of that component can be determined. Generally, substances are identified by the order in which they emerge (elute) from the column and by the retention time of the analyte in the column.

2.4 Physical components [8]

Inlet: inlet or injector provides the means to introduce a sample into a continuous flow of carrier gas.

Columns: There are two types of columns (packed and capillary) that are used in GC: packed columns which are 1.5-10 m in length and have an internal diameter of 2-4 mm. Capillary columns have a very small internal diameter, on the order of a few tenths of millimeters, and lengths between 25-60 meters are common.

Detectors: A number of detectors are used in gas chromatography. The most common are the flame ionization detector (FID) and the thermal conductivity detector (TCD). Both are sensitive to a wide range of components, and both work over a wide range of concentrations. Some gas chromatographs are connected to a mass spectrometer, which acts as the detector; the combination of both is known as GC-MS. A GC-MS can identify many of the separated compounds from the GC, since the mass spectrometer will identify the component's molecular weight but this still takes time and skill to do properly.

Methods: The method is the collection of conditions in which the GC operates for a given analysis. Method development is the process of determining



what conditions are adequate and/or ideal for the analysis required (see Figure 4). These experiments utilized a Hewlett Packard GC equipped with a J&W Scientific DB-1,30 meter, wide bore capillary column with a 1 micron film thickness and an FID detector. The column was temperature programmed from 35C (8 min) to 130C at 4C/min. hold 1 min., then to 250C at 20C/min. for 40 min. The injector and detector were held at 250C. A Hewlett Packard GC/MS 5971 mass spectrometer was utilized in the identification of soil contaminants using the NBS/Wiley probability based library search.

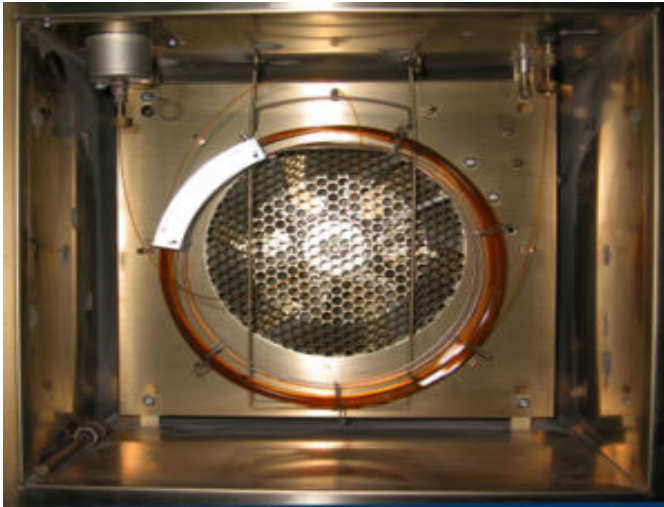


Figure 4: Picture of oven gas chromatography [9].

3 Results and discussion

Saturated Soil: Based on the concentrations of the VOCs and sulfur; the initial concentration in untreated soil was 117 part per million (ppm). After 7 cumulative days of heating, the concentrations came down by 10% of the initial, to 106ppm. After 15 days the concentrations were reduced to 103ppm that is, 12% of the volatiles were removed. After 26 cumulative days 20.51% of the compounds were removed with the concentration being 93ppm. These concentrations are plotted against time and shown in Figure 5 and the values are in Table 1. It was observed that the sulfur concentrations remain almost the same at 80ppm, throughout the heating period (0 –26 days).

Considering only VOCs, the concentrations came down to 26ppm from the initial 37ppm after 7 cumulative days of heating, showing 29% reduction. The concentrations were 23ppm and 13ppm after 15 cumulative days and 26 cumulative days of heating respectively. These values show a removal of 37% and 65% respectively. Projecting this data by a third degree polynomial it is

Table 1: Concentration of VOCs and sulfur.

| Cumulative days of heating | Total ppm |
|----------------------------|-----------|
| 0 | 117 |
| 7 | 106 |
| 15 | 103 |
| 26 | 93.5 |

Table 2: Concentration of VOCs only.

| Cumulative days of heating | Total ppm |
|----------------------------|-----------|
| 0 | 37.25 |
| 7 | 26.00 |
| 15 | 23.00 |
| 26 | 13.47 |

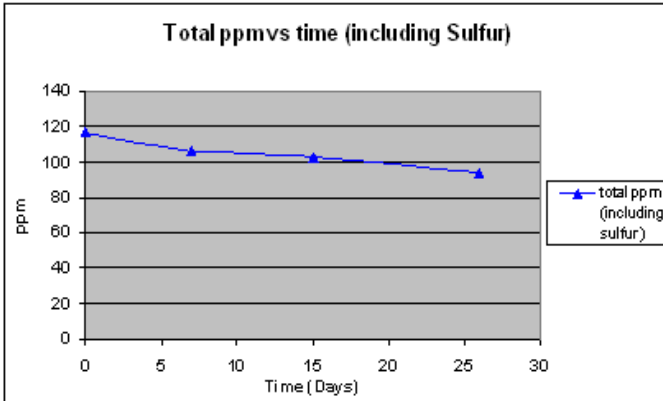


Figure 5: Graph of total ppm v/s time (including sulfur).

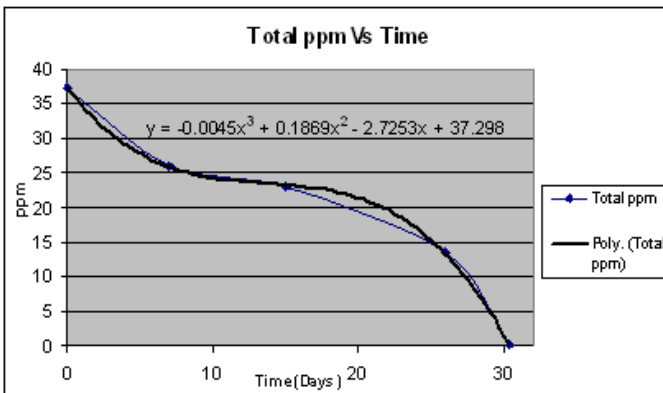


Figure 6: Graph of total ppm v/s time.

observed that, the concentrations fall below 0.37ppm (99% removal) in approximately 30 cumulative days of heating. The plot of ppm v/s time is shown in Figure 6 and the values in Table 2.

4 Conclusions

Approximately 65% of VOCs were removed in 625 hours (26 cumulative days) of heating and over 99% of VOCs are expected to be removed after 720 hours (30 cumulative days) of heating, as is shown in Figure 6. HSVE is not an effective method to remove sulfur, after heating for 26 cumulative days the concentration of sulfur remains at the same initial value. Apart from testing the effectiveness of the method, this also provides data for CFD modeling and validation.

Enhancement technologies should be considered when contaminant or soil characteristics limit the effectiveness of SVE or when contaminants are present in saturated soil. The five enhancement technologies are as follows [10]:

- Air Sparging
- Dual-phase Extraction
- Directional Drilling
- Pneumatic and Hydraulic Fracturing
- Thermal Enhancement

One of the limitations of SVE alone is that it does not effectively address contaminated soils within the capillary fringe and below the groundwater table. Among the methods listed above, air sparging can enhance the remediation capabilities of SVE in the capillary fringe zone to include remediation of chemicals with lower volatilities and/or chemicals that are tightly sorbed. This technique also enhances biodegradation of aerobically-degradable contaminants and can significantly reduce the remediation time for contaminated sites. These are the studies to be conducted as a next step.

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