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LIGHT HYDROCARBON RECOVERY USING A COMBINATION OF THERMAL AUGMENTATION AND BIOSLURPING

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Abstract

A technology for in situ soil heating combined with vacuum enhanced recovery (VER) has been developed by Golder Associates. The heating system developed is unique in its simple design, low cost and efficiency. Steel tubes (heating elements) of 6 in. diameter are inserted into the soil using standard environmental drilling equipment. The tubes heat the soils and groundwater by surface contact (conduction heating). At first, laboratory tests were performed at different scales and revealed significant increase in extraction rates for BTEX contaminated soils. In situ experiments were also performed on a gas station where a BTEX contamination was present in the soils and groundwater. Three extraction wells, seven heating elements and four monitoring points were used at this experimental site. Numerical modeling was performed using CompFlow to simulate and predict heat dispersion and multiphase flow of hydrocarbons. The temperatures reached in the soil were greater than 80°C and the recovery rates increased by 135% compared to the extraction without heating. The soils and groundwater were remediated below target levels after 5 months of heating. The spread of heat in the subsurface is not dependent on soil permeability and therefore this technology is particularly appropriate for low permeability soils such as silts and clays that are difficult to treat with other conventional technologies. To date 5 to 6 months are required to reach the desired temperature in the subsurface and a typical remediation time frame is 6 to 18 months.

Introduction

Multiphase vacuum extraction (MPVE) was implemented in the field of environmental remediation about 10 years ago. In general, the system extracts from soils the air and the liquids (water and free phase hydrocarbons) simultaneously. Although, this remediation technique has been successful in numerous cases (USEPA 1997), the recovery rates sometimes become asymptotic before reaching remediation goals.

In this context, soil heating becomes an advantageous improvement to this remediation technique and more specifically in the following situations (FRTR, 1999):

- With low permeability or heterogeneous soils;
- When contaminants are located in fractured bedrock;
- In presence of non aqueous phase liquids;
- In cold climate regions;

- With heavy hydrocarbons;
- With short remediation deadlines; and
- If aerobic biodegradation is to be enhanced.

Heating the soils alters the physical properties of the organic contaminants in soils and increases the recovery rates obtained using MPVE alone.

In 2000, a technology development program was put together by Golder Associates Ltd in order to remediate contaminated soils by heating on an active service station property. This service station is located in an urbanized area and where the presence of gasoline was observed in free and residual phases in the soils. The contaminated soils consist of sandy/clayey silt with low hydraulic conductivity, in the order of 5 x 10-5 cm/s.

The R & D project was performed in collaboration with the Montreal Centre of Excellence in Brownfields Rehabilitation (MCEBR), the Biotechnology Research Institute (BRI) which is part of the National Research Council of Canada (NRC), the Mineral Research Consortium of Quebec (COREM), the Quebec Ministry of Environment, Shell Canada Products (Shell) and HydroQuebec's Laboratory of Electrochemical Technologies and Electrotechnologies (LTEE). The duration of the project was three years and was comprised of laboratory experiments, numerical modeling work, and *in situ* experiments.

Soil heating

The objective of soil heating was to increase hydrocarbons biodegradation rate, as well as their volatilization, and to decrease the required remediation time compared with conventional vacuum extraction technique. Hydrocarbon biodegradation is influenced by soil temperature. Microbiological analyses performed during the laboratory experiments showed the presence of mesophilic and thermophilic bacteria in soils at the site. The optimal biodegradation conditions for organic contaminants is between 20 and 45°C for the mesophilic bateria and between 45 and 75ºC for the thermophilic bacteria (LaGrega *et al.*, 1994). Initially, the average temperature measured in the soils at the site was approximately 10ºC, therefore not favourable for degradation.

Heating the soils also has an effect on the physical and chemical properties of the contaminants. When an organic compound is heated, its density decreases, its vapour pressure increases, its adsorption to solid surfaces or to organic matter decreases, and its molecular diffusion in aqueous and gaseous phases increases (Davis, 1997). Moreover, the viscosity of a liquid decreases with an increase in temperature, leading to an increased migration rate of the organic compounds under a negative soil pressure. In general, there is a 1% decrease in viscosity for every degree centigrade of temperature increase.

For volatile and semivolatile compounds, the most important recovery mechanism while heating the soils is volatilization and the recovery under gaseous form, while for the heavier hydrocarbons, the recovery mechanism is governed by viscosity reduction and recovery under liquid form.

The soils on the site are contaminated by gasoline. Benzene, ethylbenzene, toluene, and xylenes (BTEX) represent the principal harmful constituents for human health and that is why soil and groundwater characterization for a site presumed to be contaminated by gasoline is often based on the presence of these compounds. BTEX have a relatively low vapour tension at 10ºC, so can only be volatilized to a certain point with traditional soil venting techniques. However, as illustrated in Figure 1, the vapour pressure of BTEX increases exponentially with temperature. A temperature increase in soils contaminated by gasoline contributes to the volatilization of BTEX and is particularly beneficial for extracting ethlybenzenes and xylenes. Heating the soils will also allow the extraction of contaminants in free phase and in residual saturation at a temperature inferior to the boiling points of the pure compounds in the different phases.

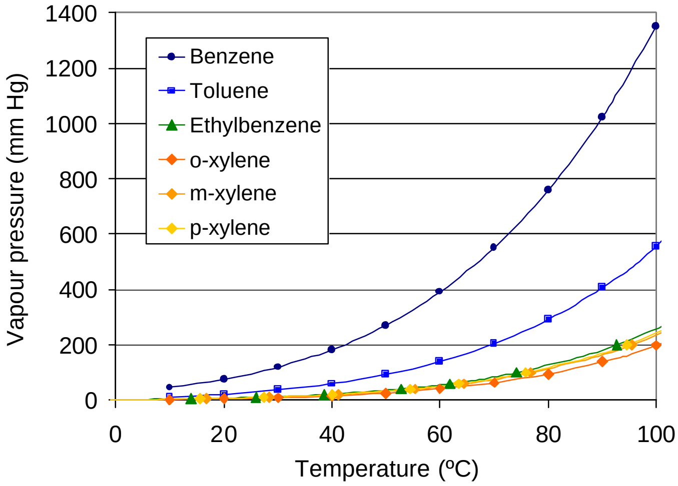

Figure 1. Vapour pressure of BTEX with relation to temperature

Heating systems

There are presently six principal methods for heating soils in situ:

- vapour injection;
- hot air injection;
- radio frequencies;
- microwaves;
- electric current; and
- thermal conductivity.

Vapour and hot air injections into the soil increase the medium's temperature and favour the volatilization of contaminants. The vapours are then removed from the soils by extraction wells under vacuum. These injection techniques are typically used for remediation of medium to high permeability soils, where the hot air and vapour can easily migrate in the soil pores, thus bringing it to a uniform temperature.

Heating by radio frequency consists of emitting electromagnetic waves into the soil to accelerate the molecular movements, thus increasing the ambient temperature. Heating by microwave is based on a similar process, but is much more intense because of the emission of higher frequencies. These two methods of electromagnetic heating can produce a rapid increase of soil temperature but they are most effective in sandy and homogeneous soils, and in soils of low water content.

Contrary to the methods previously mentioned, heating by three or six phase electric current allows for a more uniform temperature increase in low permeability or heterogeneous soils. This technology consists of inserting electrodes into the soil with a precise configuration. Each electrode is connected to a transformer that feeds the electrode with current. The heating is caused by the soil's resistance to the flow of the current generated by the electrodes. This technique is efficient, but requires a continual input of water surrounding the electrodes, because the electrical conductivity decreases in dry soils. Moreover, it may be necessary to block the access to the site during the heating period for security reasons.

Soil heating by thermal conductivity is the only technique that met all the objectives of this specific project which are to:

- develop a technology allowing to remediate low permeability or heterogeneous soils;
- use a simple and inexpensive heating method; and
- heat the soils in a safe manner and to guaranty the safety of the operational service station.

This technology is based on the principles of heat transfer in soil by mechanisms of radiation and thermal conductivity. This method is very appropriate for soils with a low to medium permeability and is barely influenced by humidity changes in the soils. Soil is a poor heat conductor, therefore requires a small amount of energy to be heated. However, the time required to achieve the desired temperatures by conduction exceeds the time required by the techniques mentioned previously.

With heating by conduction, a heat source is placed directly in the contaminated zone and very high temperatures can be achieved within the soil. It provides a simple and robust method, while requiring minimal energy (power) and was therefore chosen for the development of this technology.

Laboratory experiments

General methodology and objectives

Laboratory trials were performed at Biotechnology Research Institute (NRC/BRI) and comprised different tests on microbiology, hydrodynamics, small scale tank and bioaspiration columns tests. The microcosms and microbiological tests were performed to determine the microorganisms contribution to the mineralization of contaminants under the effect of heat. The hydrodynamic tests were used to identify the entry parameters for the numerical modeling, to define capillary properties of different hydrostratigraphic units, and to define the parameters responsible for the migration of contaminants. The small scale tank and bioslurping columns tests were performed to determine the effects of soil heating on the recovery of hydrocarbons.

Hydrodynamic tests

These tests were used to evaluate the principal properties of fluids, soils, and the interactions between the two. They also allowed drawing the typical saturation curves with respect to the capillary pressures which were used to derive the capillary properties.

The intrinsic permeability of the soils was evaluated with the hydraulic conductivity tests. It was determined to vary between 3,68 x 10-14 m2 and 5,89 x 10-14 m2 , which is typical for fine grained soils, particularly a silt.

The results of the hydrodynamic tests were used to calibrate the numerical model (COMPFLOW), and its validation was performed using the results of the small scale tank, bioaspiration column, and *in situ* tests.

Small scale tank experiment

To perform the small scale tank experiments, non contaminated soils were excavated from the site and placed in a tank located in the Biotechnology Research Institute laboratory (figure 2). Then hydrocarbons (90% Soltrol and 10% Toluene) were added to simulate the contamination present at the site. Soltrol and toluene, over gasoline, were used to ensure the worker's safety. Finally, the equipment (heating elements, extraction wells, and monitoring cells) was introduced into the tank prior to startup of the tests.

Figure 2. Soil compaction in the tank

The smallscale tank experiments consisted of three phases: a period of vacuum extraction, a period of soil heating, and a period of vacuum extraction combined with soil heating. During the period of vacuum extraction, more than 72% of the total mass was extracted (Figure 3A). At the end of this period, a significant decrease in recovery rates, for both the VOC's and the extracted liquids, indicated that the continuation of vacuum extraction would not have allowed the removal of additional mass of hydrocarbons (Figure 3B). Therefore, it was considered that the residual mass of contaminant in the soils of the tank represented, at the beginning of the period of extraction combined with soil heating, approximately 28% of the initial mass injected.

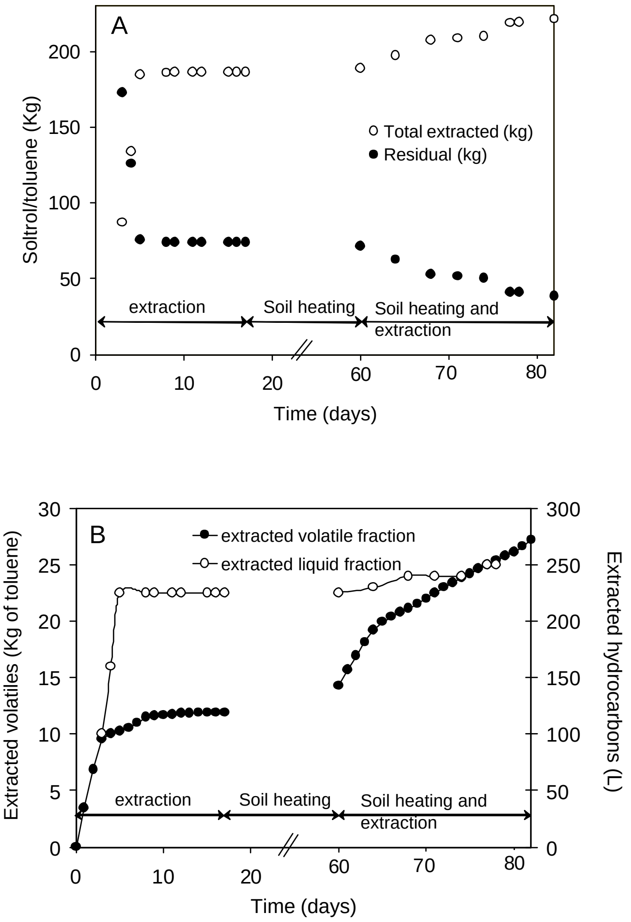

Figure 3. Hydrocarbons extracted during the small scale tank experiment. A. Total mass fraction. B. Volatile mass fraction.

The operation of the vacuum extraction system combined with soil heating allowed for the recovery of an additional 13% of the total mass of contaminants, therefore a recovery of 47% of the mass of contaminants in residual form (Figure 3B). In fact, 55% of the residual mass of toluene was extracted during this period. This also implies that the recovery of gasoline, which is a compound more volatile and less viscous than Soltrol, would have been greater than the Soltrol recovery. Therefore, soil heating had a significant effect on the recovery of contaminants in residual form.

Bioslurping column tests

The column experiments were used to characterize the hydrodynamic behaviour of gasoline and the mixture of Soltrol/toluene in the soils at three different temperatures, 20, 50, and 70ºC. The purpose of these trials was to determine the influence of the temperature on the rate of hydrocarbon recovery and on the residual hydrocarbon saturation levels.

During the experiments, 20 to 40% of the total mass of hydrocarbons was recovered (Figure 4A). The increase in temperature from 20ºC to 50ºC and then to 70ºC allowed a recovery of approximately 10% of the total mass of hydrocarbons that could not have been recovered at 20ºC. Moreover, the increase in temperature to 50ºC significantly increased the hydrocarbon recovery rate compared with the temperature of 20ºC, principally in the columns containing gasoline (C2, C5, C6, and C9) where the recovery rates increased by an average of 40% (Figure 4B).

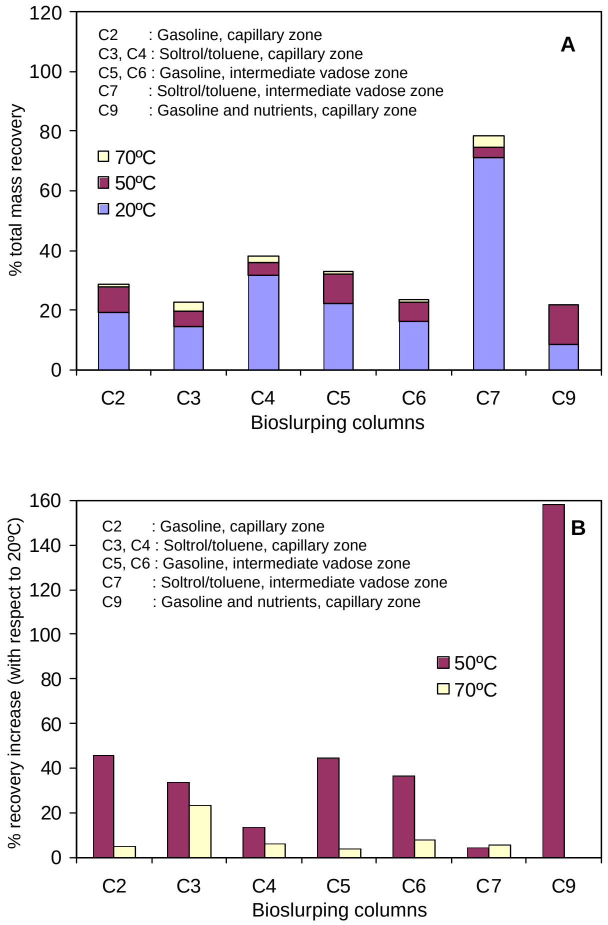

Figure 4. Hydrocarbons recovery during bioslurping column tests. A. Total mass recovery. B. % of increase versus temperature.

In situ experiments

The in situ experiments involved the installation of three extraction wells, seven heating elements, and four monitoring points, used to measure the temperature, the humidity, and the volatile organic compounds (VOCs) in the soils. The heating elements were 15 cm in diameter, 8 m in length, with only the bottom section of 3 meters providing heat with a 5000 W resistance in each of them. Figure 5 illustrates the installation of one of these heating elements.

A safety barrier, comprising 12 VOC detection wells and 12 vapour extraction wells, was put in place around the experimental area formed by the heating elements and three extraction wells to remove the hydrocarbons. The extraction wells were all connected to a treatment unit where a liquid ring pump was used to generate a negative pressure in each of the three extraction wells, therefore extracting the hydrocarbons in liquid and gaseous forms. The fluids extracted from the extraction wells were sent to an air/liquid separator. Finally, the air was treated with activated carbon before being rejected into the atmosphere and the water was sent to a sedimentation basin before being also treated by activated carbon. This entire process was automated, which allowed off site monitoring.

Figure 5. Heating element installation on site.

The in situ experiments started in May 2002 and comprised a two months extraction (without soil heating) period and a five months extraction with soil heating. During those two phases, the extracted hydrocarbon vapours concentration was measured with a VOCs detector and chemical analyses. The extracted dissolved hydrocarbons were determined by chemical analyses. The concentration of hydrocarbons adsorbed on soil was also measured by chemical analyses of soil samples collected each month.

The results at the end of the extraction period showed that there was no longer any presence of hydrocarbons in free phase in the observation wells located inside the experimental area. The results also showed that the mass of hydrocarbons extracted was principally in gaseous form. In fact, a total of 118.4 kg of hydrocarbons were extracted without heating, 8.79 kg during the heating start-up phase, and 89.85 kg during the extraction with soil heating phase, while approximately 16 g of hydrocarbons were extracted in aqueous phase (Figure 6). This confirms that the main hydrocarbon removal process is by volatilization and extraction in gaseous form by vacuum.

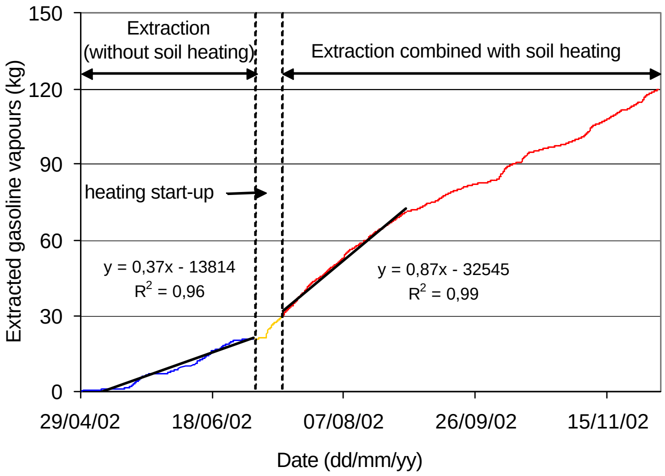

Figure 6. Gaseous hydrocarbons recovery during the *in situ* experiments.

The extraction rates were estimated from the linear regression slopes of the curves illustrated in Figure 6. The average hydrocarbon extraction rate during the extraction period was 0.37 kg/day. The rate of extraction increased by 135% with heating, at 0.87 kg/day, for the 50 days following the startup of the heating elements, illustrating the usefulness of heating the soils.

Numerical modeling

The numerical model CompFlow was used to simulate the multiphase flow of hydrocarbons. The three dimensional model simulates a three phase flow and the mass transfer between the gaseous, aqueous, and nonaqueous phases. The model was initially calibrated and validated with the field physical parameters. Then, the water and air pressures, the flows, and the saturation of the aqueous and gaseous phases, the temperatures of the soils, and the volumes of extracted hydrocarbons were simulated for the periods of vacuum extraction and vacuum extraction combined with soil heating. Figure 7 shows the temperatures obtained in the soils after 130 days of heating, according to the CompFlow model.

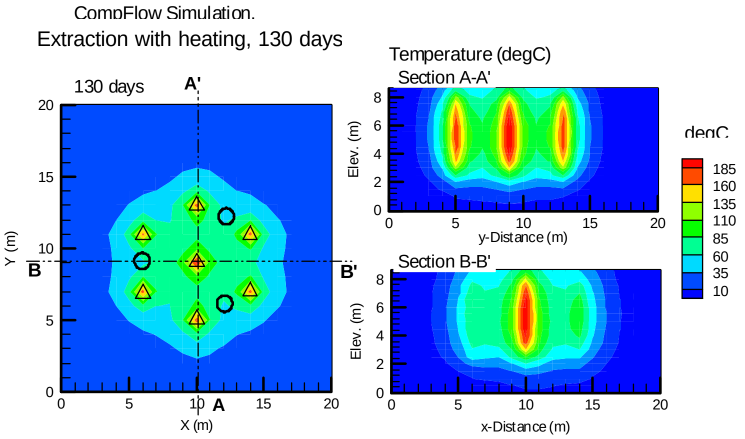

Figure 7. Simulated temperatures (130 days of vacuum extraction combined with soil heating)

The volumes of extracted hydrocarbons simulated were close to the volumes actually recovered on the field during both periods of extraction. However, the extraction rate simulated for the vacuum extraction with soil heating period was slightly overestimated compared to the actual rate observed in the field (Figure 8).

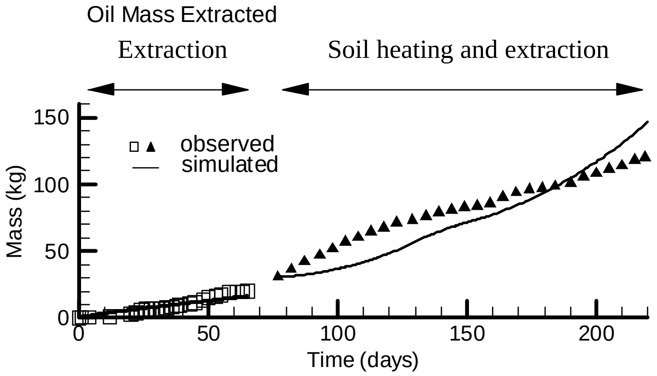

Figure 8. Observed and simulated extracted hydrocarbons mass.

Efficiency of the heating system by thermal conduction

The heating elements were in operation for approximately 5 months. During this period of heating, the inputted temperatures were increased gradually to 200°C and the soils reached, at the end of the trial period, an average temperature of 80ºC in the centre of the experimental area.

The soils temperatures reached in steady state are independent of the soils thermal properties and are determined by the temperature setting of the heating element. The results obtained from the numerical model showed that for a temperature setting of 200ºC at the heating element, a temperature of 100ºC would be reached at steady state by the soils located in the centre of the experimental area. The temperatures reached after 145 days of soil heating, which are around 80ºC, represent 72% of the steady state temperature.

The time to reach steady state depends on the soils thermal diffusivity and is independent of the temperature setting of the heating elements. The numerical model showed that 1000 days would be necessary to reach the steady state. The time constant, which represent the time to reach 66% of the steady state temperature (73ºC in this experiment), is approximately 80 days for this site. The objective of using a soil heating system is not to reach steady state, but to determine a heating setting of the elements that allows reaching the desired temperature in one or two time constants (80 to 160 days). The numerical model showed that a 275ºC temperature setting of the heating elements would allow the soils to reach 100ºC in 80 days and the hydrocarbons recovery rate would then be increased in comparison with the rate obtained in this study.

Microbiology

The bacterial counts performed on the soil samples collected on the site indicated the presence of a small bacterial population. Probable reasons for low bacterial populations include a surrounding basic pH (~9) and a weak nutriment concentration in the soils. Nevertheless, the indigenous alcalinophil bacterial populations, capable of living in this type of soil, were present. Molecular analyses also confirmed the presence of hydrocarbonoclast bacteria. Microcosms experiments indicated that the biodegradation was probably limited by the low nutrients contained in the soils and that adding fertilizers could favour biodegradation.

During the tank experiments, no significant effect was noted on the increase in microbial activity during the heating period. During the bioslurping column trials, the addition of fertilizers increased the mineralization of toluene and the number of mesophilic population during the bioslurping phase without heating. However, during the bioslurping phase with heating (50ºC), the mineralization was almost completely inhibited and the number of mesophilic bacteria decreased significantly.

The microbial analyses conducted during the *in situ* experiments indicated that the soils affected by hydrocarbons had a low microbial population. The mineralization trials and the screening of bacterial columns with a xy/E probe marked with dioxygenine did show a bioremediation potential only when nutrients were added to the medium. The rate of mineralization in microcosms with the addition of fertilizers was relatively high for the soil samples during the vacuum extraction period and for the vacuum extraction with soil heating period for soils where the temperature did not exceed 45ºC. However, there was no increase in the mineralization under the effect of heating soils.

It is important to note that the estimates of mineralization in microcosms are generally overestimated and that the injection of nutrients in the soils at the site would not necessarily result in an increased mineralization rate. Considering the presence of free phase products, the addition of a nutrient solution would require the injection of an important quantity of water, which was not desired.

Conclusions

The in situ trials confirmed that the developed soil heating treatment technique did favour the volatilization of hydrocarbons present in the soils which were removed by vacuum enhanced recovery. The results obtained with the in situ experiments confirm the benefits of implementing a heating system combined with a vacuum extraction system for sites where the soil permeability is low. In fact, it clearly demonstrated that heating soils decreases the treatment time, increases hydrocarbon recovery rates compared with traditional extraction technologies.

The use of such heating technology can also be applicable and beneficial for other types of contaminants, besides light hydrocarbons. In fact, when an organic compound is heated, its recovery under negative pressure is increased. The heavier contaminants will be recovered principally in liquid form, while volatilization and recovery in gaseous forms is the main mechanism for light contaminants.

Also, the study showed that heating increases the costs of construction and installation of a treatment system by about 40 to 50% and, onwards, the operational costs by 15 to 20%. Although this technology increases the initial and operational costs compared with conventional treatment, it remains financially attractive because it significantly reduces the treatment period, thus becoming more reliable and economic.

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