

In-Situ Thermal Treatment of NAPL Floating Layer: Application of Thermopile©

“Traitement thermique in-situ d’une couche flottante: Application de Thermopile©”

Dr Hatem Saadaoui, Ir Ugo Falcinelli, Ir Jan Haemers
Deep-Green SA – 245, Av. Montjoie – B-1180 Brussels (Belgium)

SUMMARY

Thermopile©, (patented by Deep-Green) is a new thermal treatment technology which, without the need for excavation, uses the desorption of volatile products from polluted soils. The technique uses the combustion gases (in quasi closed-loop gas circuit) to heat the soil and recuperate the contaminant. The circuit consists of a unit of combustion, a fan, a network of pipes and a purge. The technique has already been successfully applied on several urban and industrial sites. Thermopile© in-situ was recently used on the sites of D’Ieteren in Brussels for the treatment of a floating layer of 50cm thick (on average) located at a depth of 2.5m. The area of the zone treated is ~5m². The achieved results are very promising.

KEYWORDS

NAPL, in-situ thermal treatment, floating layer

I - Introduction

NAPL ‘Non-Aqueous Phase Liquids’, such as petrol products and volatile organic solvents, are the main pollutants of soil and underground water. The pollution of soil by these products is generally accidental and is caused by several sources, such as leaks from reservoirs and pipes of exterior or underground storage, pools of oil, or chemical waste deposits.

Once present in the soil, these products tend to move downwards under the effect of weight and leaves in its path some residual quantities [1-3].

A floating layer appears when the NAPL (lighter than water) reaches the underground water. The liquid accumulates in the saturated zone, just above water.

The treatment of a floating layer and / or the saturated zone presented several difficulties:

- Difficult to access: generally, the polluted area is located at significant depths, thereby making intervention difficult and costly.

- Presence of large quantities of water: the presence of water limits the effectiveness of the intervention (longer processing time, the persistence of pollution in the saturated zone, etc.).

Excavation, pumping (“pump and treat”) and skimming, are the most well-known methods used to treat the floating layer. However, these methods are costly, not completely efficient and not always physically possible [4].

In-situ thermal treatment is an alternative method. In effect, heating the soil leads to dramatic changes in thermodynamic conditions and makes the contaminant much more mobile. The main effects are:

- The vapour pressure of the contaminant increases significantly with temperature. Heating soil from the ambient temperature to 100°C increases more than ten-fold the vapour pressure of the contaminant and improves the mass transfer liquid→gas.

- In areas where the contaminant and water are present, the boiling of the mixture occurs at temperatures below 100°C. For example, a mixture of water and trichlorethylene (boiling point: 87°C) boils at 73°C.

- The contaminant desorption from soil increases with temperature.

- As temperature increases, the viscosity, the liquid density and the interfacial tension between contaminant and water decrease. This promotes the movement of the contaminant.

Thermopile© is a new In-Situ Thermal Treatment method. It has been applied successfully on the D'leteren site in Brussels. The soil is contaminated with mineral oil and a floating layer of 50cm thick (on average) located at a depth of 2.5m.

2 – Thermopile©, [5-6]

Thermopile© is a technology based on thermal conduction that can effectively reach organic contaminants in-situ, independently of large soil heterogeneity. As with all thermal desorption technologies, Thermopile© reaches very low levels of organic contaminants (background levels), thereby releasing the site owner of any future liability, including the monitoring, reporting, follow-up or potential future clean-up of residual saturation.

The technology consists of a network of steel pipes driven into the soil, in which hot gases are circulated. The pipes are doubled (with an inner tube where hot gases enter and an annular zone – between both tubes – where the gases exit the pipe). The outer pipes are perforated and, as such, create a negative pressure in the whole zone to be treated. The negative pressure and the heat conduction in the soil lead to the migration of all the volatilized organic contaminants into the pipes.

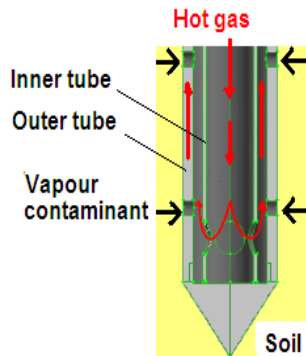


Fig 1. Heating pipe

At the surface, the vapour organic contaminant is then brought into a thermal oxidizer where it is destroyed. The combustion gases (approx. 850-900°C) are then re-circulated in pipes. The whole circuit is a quasi-closed loop.

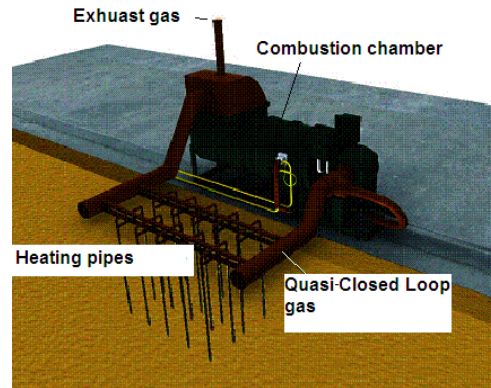


Fig 2. Thermopile© in-situ

The technology has been applied in-situ at different sites where organic contaminants (such as fuel oil, diesel, PAH, coal tars, etc.) were present and demonstrated clean-up levels down to standard levels (< 10 mg/Kg_dm for Total Petroleum Hydrocarbons, for example), starting from very high concentrations (above 30,000 mg/Kg_dm), in a few weeks.

- The system is also particularly fuel-efficient, consuming much less energy per ton treated than traditional thermal desorption (more than five times less). This fuel efficiency can be explained by two main factors:

1. Quasi-closed loop circuit – This allows the whole hot gas flow to be reused and avoids high temperature flow gas release, resulting in increased energy efficiency. In this case, all gases are re-circulated and only a very small purge gas flow, of which 70% of the energy is recuperated, is released into the atmosphere.

2. The organic contaminants in the soil are used as fuel. By desorbing all organic contaminants, Thermopile© uses them in the gas flow as a source of energy. All desorbed gases are sent to the oxidizing chamber, where they are burned to produce high temperature gases. These hot gases are then sent into the system in order to continue to heat up the soil.

In addition to the in-situ and energy

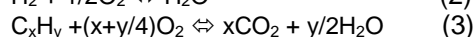
efficiency benefits, Thermopile© in-situ represents a leap forward in the environmental impact of thermal technologies. It reduces CO₂ emissions, as well as total gas emissions (SO₂, NO_x, etc.). No dust emissions, thanks to the specificity of the process where manipulation of soil is no longer carried out. Also local disturbances are much lower than with traditional technology, as no moving parts are present in the system to handle the soil (screening, rotary kiln, etc.) and therefore noise and odours are almost inexistent.

Moreover, the treatment is fast (expressed in weeks, mobilisation and demobilisation included).

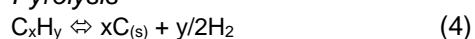
3 – Physical and chemical mechanisms

When soil is heated, organic components are vaporised and directed towards the pipes. The majority of the components are thus destroyed in-situ in the superheated zone near each pipe (oxidation and/or pyrolysis reactions). The remaining quantity is destroyed in the gas circuit and in the thermal oxidizer, where the temperature exceeds 850°C.

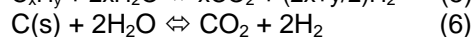
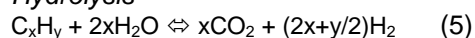
Oxidation



Pyrolysis



Hydrolysis



Steam distillation

Due to the molecular weight of water, water vapour is more efficient for the evaporation of organic compounds than air.

When temperature reaches the boiling point of water, steam distillation of organic compounds occurs.

For non-miscible liquids the mass fraction of a compound in the vapour phase is expressed as followed:

$$y_i = \frac{1}{1 + \frac{M_1 P_1^0}{M_i P_i^0} + \dots + \frac{M_{i-1} P_{i-1}^0}{M_i P_i^0} + \frac{M_{i+1} P_{i+1}^0}{M_i P_i^0} + \dots + \frac{M_N P_N^0}{M_i P_i^0}}$$

The Clapeyron law gives the saturation vapour pressure:

$$\ln P_i^0 = A_i + \frac{B_i}{C_i + T}$$

For a binary mixture (e.g. C_xH_y/Water), the mass fraction is:

$$y_{C_xH_y} = \frac{1}{1 + \frac{M_{eau} P_{eau}^0}{M_{C_xH_y} P_{C_xH_y}^0}}$$

The following table gives the mass fractions of water / organic compound at 100°C.

Compound	T _b (°C) at 1atm	M _{C_xH_y} (g/mole)	T(°C)	y _{C_xH_y}
Benzo-cyclopentane (C ₉ H ₁₀)	177	118	100	0.406
n-Hexadecane (C ₁₆ H ₃₄)	287	226	100	0.011

Table 1. Vapour mass fractions of water/Benzo-cyclopentane and water/n-hexadecane at 100°C.

The partial pressure of miscible compound is given by Raoult's law.

4 – Case study: treatment of the D'leteren site

D'leteren Auto (Kortenbergh, Brussels) is an international Belgian company, occupying a significant share of car distribution activities in Belgium. Following many years' activities involving the use of organic products on the company's site (cleaning cars, treatment of car bodies, etc.), a high quantity of organic compounds was leaked into the soil. A floating layer formed at a depth of 2.5m above the underground water. This layer, with a variable height of 20-80cm dependent on the place, was spread over a surface of 2000m². In addition to the floating layer, the soil and water analyses revealed the presence of mineral oils, the BTEX and the PAH (cf. table 2).

To rehabilitate the site, D'leteren requested Deep-Green SA to carry out an in-situ Thermopile© test.

The principal objective of this test was to evaluate the effectiveness of the

technology and to estimate the time and the cost of treatment.

Soil and water pollution

Pollution is composed of a mixture of mineral oils, BTEX and a lower quantity of PAH. The following table shows the results of analyses carried out on soil and water samples taken before treatment.

Sample	BTEX (mg/Kg-dm)	C10-C40 (mg/Kg-dm)	PAH (16) (mg/Kg-dm)
Soil (at 1m)	<0.25	97.4	0.06<x<0.81
Soil (at 2m)	<0.25	---	<0.8
Soil (at 4m)	<0.25	848	1.46<x<1.91
Sample	BTEX (µg/L)	C10-C40 (g/L)	HAP (16) (µg/L)
Liq(water)	414	1.3	740

Table 2. Soil and water pollution

5- Thermopile© installation

The Thermopile© installation, used for this test, comprises 3 vertical heating pipes (each one 4m in length). These pipes are placed in equilateral triangle with a distance of 1.5m. The total area of the treated zone was 5.3m². The external tubes are placed at a depth of 4m (soil level). To avoid water in tubes, perforations are not made in the drowned part (high 1.5m). The internal tubes are placed at a depth of 3.5m (soil level). All are connected to a network of the horizontal tubes (for the circulation of gases), to the post-combustion (maximum power 40KW) and to the fan (cf. figure 3).

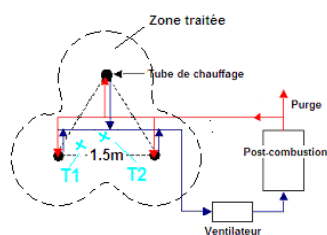


Figure 3. Thermopile© installation at D'Ieteren site

Heat insulation and escaped gas treatment

To reduce heat loss, all system and soil surfaces were insulated. A 15cm layer of concrete was laid on the soil. This layer prevented the emission of gas from soil into the atmosphere. In addition, the system was protected with a high temperature (250°C), watertight resistant

covering. The gases collected were sucked into and passed through granulated activated carbon before being released into the atmosphere.

Temperature measurement

A total of 7 type K thermocouples were located in the soil at different depths (Figure 3). The depths were 1, 2, and 4m respectively.

In addition, 8 thermocouples were placed on the gas circuit at the entry/exit of the pipes, on the feed gas line, in the thermal oxidizer and before the fan. The data logger used was the Microlink 751. The temperatures were recorded every 10 minutes.

Gas analysis

The gases were analysed using an MRU Variousplus. Daily samples of gas from the fan line, the thermal oxidizer and stack (purging gas) were taken. The gases analysed are NO_x, CO, CO₂, O₂, SO₂ and HCT.

Floating layer

To follow the evolution of the floating layer, 3 wells with a depth of 5m were dug – one at the centre and the two others at the outside of the treated area (at 1 and 5m from the installation).

Thermal oxidizer control

The most important parameter of the treatment is the combustion gas temperature and the oxygen concentration in the gas circuit. The parameter values chosen should allow for a greater combustion yield and a higher inlet pipe gas temperature. The automatic setting of the burner air and fuel ratio guarantees a constant temperature at the exit of the thermal oxidizer and the oxygen concentration.

Process control system

Given the lengthy treatment time, the installation was equipped with an automatic control system. This system supervises gas temperature and pressure, the gas emitted and the air-site quality (confined space). If the limited values are exceeded, the installation is stopped following an automatic sending of an alert message by SMS.

Treatment time

Based on the energy and mass balances, the treatment time was estimated at

60 days. The heating began on August 4, 2008 and continued until October 13, 2008.

6- Results and discussions

Temperature

The following figure gives the soil temperature.

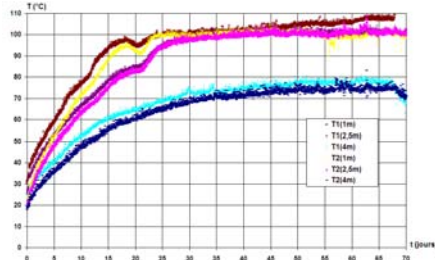


Fig 4. Soil temperature

We can clearly observe two heating phases:

- A first phase of 20 days, during which soil temperature rises to 100°C (boiling point of water).
- A second phase of 50 days, during which the soil temperature (except for the zone close to pipe) remained at the boiling point of water (100°C). During this phase the energy yielded to the soil is used for the evaporation water and contaminants. The superheated zone close to pipes ($T \gg 100^\circ\text{C}$) is a form of well, which accelerates the drainage and the elimination of the floating layer (cf. Figure 5).

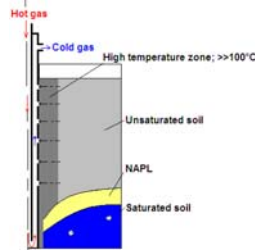


Fig 5. The superheated zone close to pipes ($T \gg 100^\circ\text{C}$) resembles a well.

Evolution of the floating layer

During the treatment, and to follow the evolution of the floating layer, measurements are taken in the control wells. Only the central well showed a reduction in the floating layer; after 70 days of treatment it became non-existent (cf. Figure 6).

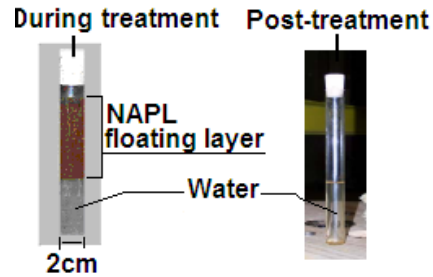


Fig 6. Liquid samples from the central well (during and after treatment)

Soil and water analysis

Different soil and water samples were taken before and after treatment. The samples were analysed in an approved laboratory (Eurofins Analytico). Analyses results are shown in Table 3.

Sample	BTEX (mg/Kg-dm)	C10-C40 (mg/Kg-dm)	PAH (16) (mg/Kg-dm)
Soil (1m) Pre-treat.	<0.25	97.4	0.06<x<0.81
Soil (1m) Post-treat.	LD	<50	<0.1
Soil (2m) Pre-treat.	<0.25	NA	<0.8
Soil (2m) Post-treat.	LD	240	<0.05
Soil (4m) Pre-treat	<0.25	848	1.46<x<1.91
Soil (4m) Post-treat.	LD	180	<0.8
Sample	BTEX (µg/L)	C10-C40 (g/L)	PAH (16) (µg/L)
Liq(Water) Pre-treat.	414	1.3	740
Liq(Water) Post-treat.	<40	0.007	<11

NA: not analysed; LD: Low than detection; dm: dry matter.

Table 3. Pollution levels (soil and water) before and after treatment.

After treatment, all water and soil analyses results show a high reduction of contaminant concentration. The results also show the elimination of BTEX and the reduction of PAH in water.

7- Conclusion

The results obtained at the D'leteren site show the effectiveness of the Thermopile® in-situ thermal technology in treating the NAPL floating layer. With a distance between pipes of 1.5m and after 70 days of heating the floating layer is almost non-existent. The steam water distillation and the contaminant destruction (by several chemical reactions) in the superheated zone close to pipes ($T \gg 100^\circ\text{C}$) constitute the principal mechanisms of treatment.

Nomenclature

M_i :	Compound molecular weight [Kg/mol]
P° :	Saturation Pressure [Pa]
T :	Temperature [K]
y_i :	Compound mass fraction (gas phase)

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