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Title of abstract	**MATHEMATICAL MODELING OF THERMAL CONDUCTION IN SOIL IN PRESENCE OF NON-AQUEOUS PHASE LIQUIDS FOR THE THERMOPILE© PROCESS DESCRIPTION**		
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MATHEMATICAL MODELING OF THERMAL CONDUCTION IN SOIL IN PRESENCE OF NON-AQUEOUS PHASE LIQUIDS FOR THE THERMOPILE© PROCESS DESCRIPTION

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Abstract
Thermopile©, a new polluted soil thermal treatment method, has been patented by Deep Green. The process uses heat by conduction and vacuum in closed gas loops to clean soil polluted by a range of organic compounds. The system comprises a thermal oxidizer with purge, a fan and heating pipes (perforated tubes). To describe the Thermopile© process, a one-dimensional multi-component, non-isothermal model has been developed. The system considered is formed with one heating pipe surrounded by soil. The Pendular Rings approach has been used to characterise the residual saturation of NAPL (Non Aqueous Phase Liquid). This model can be used to help us to evaluate the cost and the processing time and to improve the performances of the Thermopile© process.

Introduction
The contaminants most frequently detected in soil are known as NAPL (Non Aqueous Phase Liquid). These liquids include chlorinated fuels (oil derivatives), solvents, oils (e.g. engines) and tar. In the USA 52 of 77 contaminated sites were polluted by the NAPL [1].
Several sources are responsible for soil contaminate: escapes from tanks and piping of storage external or underground, oil puddle pools, provisions of chemical waste [2]. The majority of these organic liquids have a low volatility and are not miscible in water. When present in soil, they tend to persist in the environment as a distinct phase, which can be used as a long-term source of air and water contamination. While it moves to the bottom by capillary action, part of the liquid is maintained in the matrix of soil. This part is known as the residual NAPL. Residual saturation varies according to soil characteristics [3-6].
Thermopile©, a new polluted soil treatment method, economical and environmentally friendly, and based on thermal desorption, has been patented by Deep Green. The technology consists of installing stainless steel pipes in the soil, in which hot gases are circulated. The system (quasi-closed loop) comprises a thermal oxidizer with purge, a fan and heating pipes (perforated tubes). During the treatment, gases at high temperature (>500°C) coming from the thermal oxidizer move along the tubes and heat the soil by conduction. The evaporation of contaminants occurs when the soil reaches high temperature. The vaporized constituents are drawn toward the holes, thanks to the negative pressure created by the fan, and they are rapidly destroyed in the soil before reaching the tubes due to the high soil temperature (oxidation and pyrolysis reactions). The remaining vapours are destroyed in the thermal oxidizer. The device is equipped with a purging, making it possible to regularly evacuate a small part of gases and to keep the same pressure and oxygen level in the system. The burner is also equipped with an auxiliary feed of fuel and air. The efficiency of the Thermopile© process is due to an optimal use of energy; the small amount of energy contained in the purge-gas is used to heat the burner-air and the cold gas loop flow at the inlet of the thermal oxidizer.

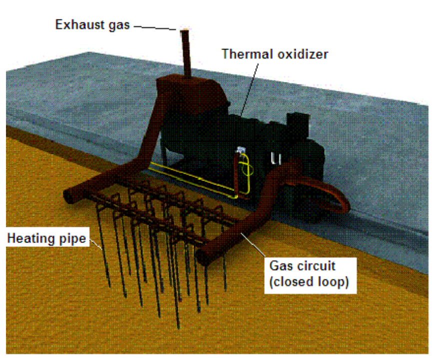

Fig 1. Thermopile© in-situ system

Thermopile© can be applied on all kinds of soils polluted by organics constituents, such as coal, tar, petroleum fuels, chlorinated solvents and oils.

To describe the Thermopile© process a mathematical model has been developed. The system considered is formed with perforated tube surrounded by a thick soil layer (figure 2).

Modelling work

We consider the situation represented in Figure 2, in which the grey area represents the contaminated soil and hatched line the perforated tube.

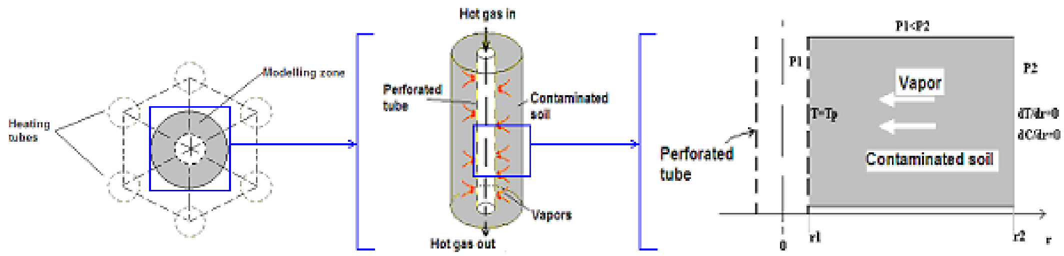

Fig 2. Modeling area and boundary conditions.

The model is described by the four equations: yhe mass conservation equation for fluids in soil, the Darcy law for motion of fluid in soil, the heat balance equation for soil and fluids and the species conservation equation.

The Pendular Rings approach was used to characterise the residual saturation of NAPL. In the literature, several expressions exist for the volume of the ring and the surface of the interface between the liquid and gas. Femlab and Matlab softwares are used for calculation. To validate the model the results are compared with the experiments results of Lingineni [7].

Model Assumptions

1) The pollutant (in residual saturation) is uniformly distributed in the soil.
2) No movement of liquids and solid.
3) No temperature difference between solid and fluids.
4) No axial temperature difference.
5) The soil structure remains constant and soil properties such as bulk density and total porosity are homogeneous.
6) The gas flow in the soil is dominated by the viscous forces and can be described by the Darcy law.
7) No gravity effect on gas motion.

Model Equations

According to above assumptions, material balance and mass transfer, mass conservation of fluids and the energy balance equations were obtained as:

Mass conservation equation:

$$\frac{\partial\left(\varepsilon\rho_g S_g\right)}{\partial t} + \nabla.\left(\varepsilon_g \rho_g U_g\right) = \sum_i \dot{m}_{i,l\to g}$$

The perfect gases law gives the density of gas:

$$\rho_g = \frac{\left(M_{air} y_{air} + \sum_i M_i y_i\right) P}{RT}$$

The equation of motion for gas flow in soil, as described by Darcy's law, can be written as:

$$U_g = -K \frac{k_{r,g}}{\mu_g} (\nabla P)$$

The permeability of gas varies according to gas saturation as follows:

$$k_{r,g} = S_g^3$$

Darcy's law must be substituted into the mass conservation equation to obtain the equation of pressure:

$$\frac{\partial\left(\varepsilon\rho_g S_g\right)}{\partial t} + \nabla.\left(-\varepsilon_g\rho_g K\frac{k_{r,g}}{\mu_g}\left(\nabla P - \rho_g g\right)\right) = \sum_i \dot{m}_{i,l\to g}$$

The mass conservation of a compound *i* in the gas phase is given by the following equation (i=1,2…,n):

$$\frac{\partial C_{i,g}}{\partial t} + U_g.\nabla C_{i,g} - D_{i,g}\nabla^2 C_{i,g} = \dot{m}_{i,l\to g}$$

The mass conservation of the liquid phase is given by the following equation:

$$\frac{\partial\left(\varepsilon\rho_l S_l\right)}{\partial t} = -\sum_i \dot{m}_{i,l\to g}$$

The gas and soil temperatures can be assumed to be equal. This assumption is based on the fact that the transfer area available for heat transfer is quite large for packed beds of small particles. The energy balance is given by the following equation:

$$\left(\rho C_p\right)_m \frac{\partial T}{\partial t} = \lambda\nabla^2 T - \left(\rho C_p\right)_g U_g \nabla T - \sum_i \dot{m}_{i,l\to g} h_{l\to g} + \dot{m}_{eau,g\to l} h_{eau,g\to l}$$

Initial and boundary conditions

The following initial and boundary conditions are applicable for the situation represented in Figure 2, in which the grey area represents soil. The circulation of gas is created by application of a vacuum pressure inside the tube (r=r1):

$$t = 0 \quad \forall r; \quad P(0,r) = P_{atm}; \quad T(0,r) = T_{amb}; \quad C_i(0,r) = C_{i,sat}(T_{amb})$$
$$S_l(0,r) = S_{o,l}; \quad S_g(0,r) = 1 - S_{o,l}$$

$$r = r_1 \quad \forall t; \quad P(t,r_1) = P_1 < P_{atm}; \quad T(t,r_1) > T_{amb}$$

$$r = r_2 \quad \forall t; \quad P(t,r_2) = P_2 = P_{atm}; \quad \frac{\partial T(t,r_2)}{\partial r} = 0; \quad \frac{\partial C_i(t,r_2)}{\partial r} = 0$$

We can easily change the boundary conditions and study different configurations.

Mass transfer liquid/gas

The principal mechanisms of mass transfer in a multiphase system are presented in Figure 3.

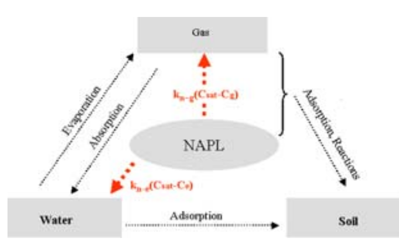

Fig 3. Possible mechanisms of mass transfer between various phases.

The following law gives the rate of mass transfer between liquid and gas phases:

$$\dot{m}_{N\to\alpha} = k_{N\to\alpha} A\left(C_{eq,\alpha} - C_\alpha\right)$$

$k_{N\text{-}\alpha}$ is the coefficient of mass transfer, *A* is the mass transfer surface per unit of total volume and $C_{eq,\alpha}$ and C_{α} are respectively the vapour equilibrium concentration of contaminant in α phase and the real concentration of the contaminant in the α phase.

The mass transfer coefficient can be estimated from the relation of Sherwood [8], valid for mass transfer in packed beds of spheres and cylindrical pellets with single fluid flow.

$$k_{N\rightarrow\alpha} = 1.17U_g \mathrm{Re}^{-0.415} Sc^{-2/3}$$

During the treatment, the evaporation of the contaminant reduces the surface of mass exchange between liquid and gas. To take account of this variation, Rose [9] presented a method to determine the volumes and surface areas of liquid for different saturations in solid matrix.

Surface exchange, *A*. Pendular Ring approach

When the saturation values of the liquid contaminants are equal to or less than the residual saturation, a pendular configuration of liquid is supposed to exist in the soil. Figure 4 presents this configuration. The approach used to characterise this configuration is called a model of Pendular Rings. It describes the geometry of the liquid in the porous environment like rings of liquid formed around the points of contact between solid particles.

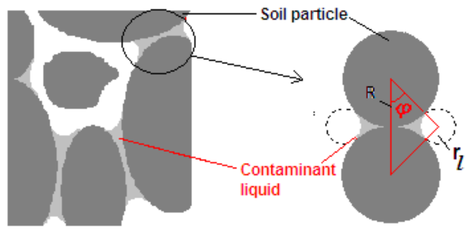

Fig 4. '*Pendular Ring'* Approach [9]

Assuming that the interfacial surfaces of the pendular rings can be regarded as arcs of circles, the volume of one pendular ring that forms a zero contact angle can be determined according to the equation [10]:

$$V_{ring} = 2\pi R^3 \left\{ 2 - 2\cos\varphi - \mathrm{tg}\varphi \left[2\sin\varphi - \mathrm{tg}\varphi + \left(\frac{\pi}{2} - \varphi\right)\left(\frac{\cos\varphi - 1}{\cos\varphi}\right)^2 \right] \right\}$$

The surface exchange liquid/gas of a ring is given by:

$$S_{ring} = 4\pi R^2 \left(\frac{1-\cos\varphi}{\cos\varphi}\right)\left[\left(\frac{\pi}{2} - \varphi\right)\mathrm{tg}\varphi - (1-\cos\varphi)\right]$$

Figure 5 Shows the variation of Liquid/Gas surface exchange per unit volume of the porous media, A, according to the residual saturation of the liquid.

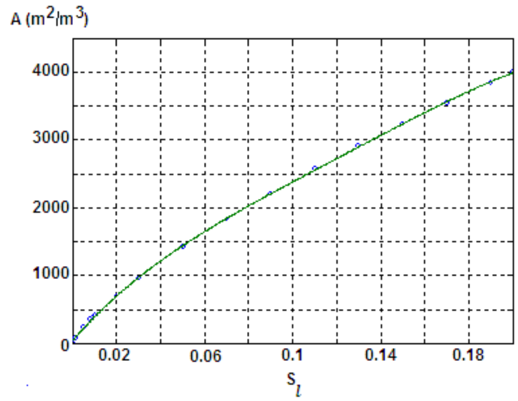

Fig 5. Liquid/Gas surface exchange per unit volume of the porous media versus liquid saturation.

Model Results

First we will present a typical validation result of the model with experiments found in the literature and then we will give some examples of model results for our system.

Model validation

The validation of the model was carried out thanks to the experiments of Lingineni [4]. These experiments were carried out on a rectangular column of section (18cmx18cmx60cm) filled with 360µm diameter glass spheres. Ethyl-alcohol was used as a single component contaminant at a residual saturation of 13%. A flowmeter followed by a vacuum pump are connected in bottom. The top of column is remained free. For the temperature measurement of the soil, several thermocouples are placed along the column. A gas chromatograph is used to analyse the various samples taken along the column. The temperature is recorded every 30s.

An example of the experimental results is presented in Figure 6. The experiment is carried out with a constant ambiant airflow of 0.234 m^3/min.

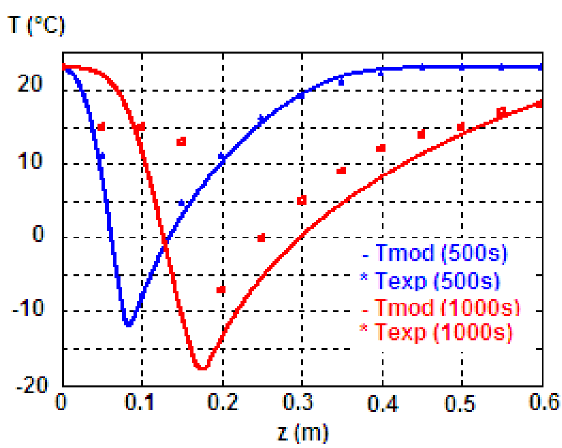

Fig 6. Comparison of simulated and measured axial temperature profiles at t=500 and 1000s.

The mathematical model correctly predicts the local reduction of soil temperature and gives satisfactory results; the circulation of air in the soil starts the evaporation of the contaminant (ethyl-alcohol). This evaporation occurs at the Liquid/Gas interface. Due to the high surface area per unit volume of the porous media, air becomes saturated with contaminant vapour within a narrow region. This last operation reduces the temperature of the soil in the region where evaporation proceeds. The temperature of the soil continues to decrease until an equilibrium condition is reached between the heat transfer from the incoming air to the soil and the evaporation heat or until all contaminants at the location have been completely evaporated. After total evaporation of the contaminants, the temperature of the soil increases again thanks to heat coming from the air.

Model applications

The mathematical model described above is written for the symmetric-radial system presented in Figure 2. The system consists of a heating tube 9cm in diameter surrounded by approximately 35cm thick sand layer. The remediation of the sand contaminated with various volatile compounds was investigated. The contaminants are benzene and/or o-xylene. Table 1 gives the physical and chemical properties of contaminants and the characteristics of soil.

		benzene	o-xylene	Sand (d_{50}=500µm)
	$MMx10^3$	78.10	106.16	---
	$\rho_{l,20°C}$	870	880	ρ_s=2200
Antoine's equation:	aa	14.16	14.12	---
$P(bar)=10^{-2}\exp\left[aa-\frac{bb}{cc+T(K)}\right]$	bb	2948.78	3412.02	---
	cc	-44.56	-58.68	---
	$h\ x10^5$	3.935	3.465	---
	Cp_s	---	---	850
	K	---	---	10^{-12}
	λ_s	---	---	0.78

Table 1. Physical and chemical properties of contaminants and soil characteristics

The contaminant residual saturation is fixed at 15%. The temperature of the wall (at r=r1) is T_s=400°C. All simulations is conducted with a constant drop pressure of (P_2-P_1)=1000Pa.

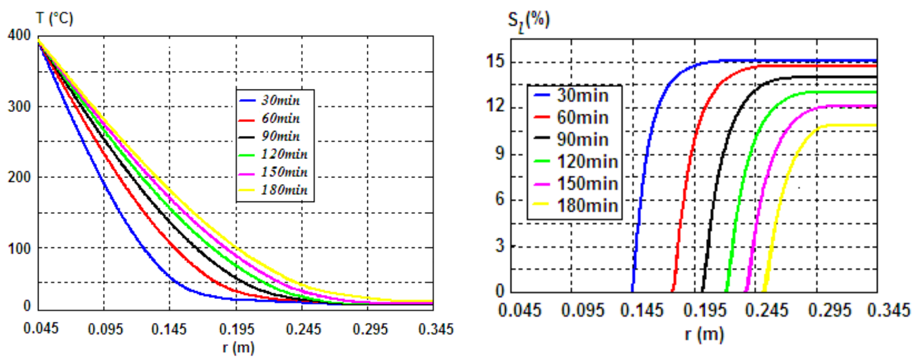

Fig 7. Simulated soil temperature and benzene liquid-saturation profiles at various time (S_l=15%, T_s=400°C, P_2-P_1=1000Pa).

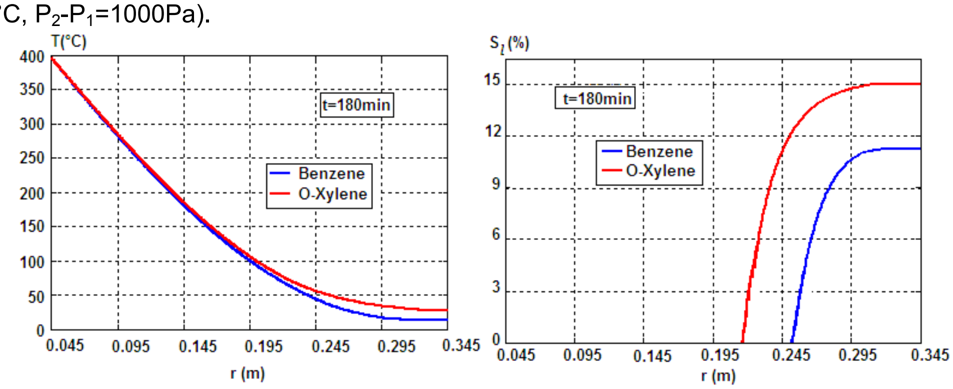

Fig 8. Simulated soil temperature, benzene and o-xylene liquid-saturation profiles after 180min (S_l=15%, T_s=400°C, P_2-P_1=1000Pa).

Conclusion

A one-dimensional non-isothermal, multi-compound model was developed and has been used to describe heat conduction and contaminant evaporation in soil. The validation of the model is carried out thanks to the experiments of Lingineni [4]. To describe the Thermopile© system more accurately, chemical reactions (e.g. Thermal oxidation, Pyrolisis, etc.) should be taken into account.

Acknowledegments

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Nomenclature

A	total surface of mass exchange liquid-gas per unit volume [m^2/m^3]
C_i	compound concentration in the gas phase [Kg/m^3]
Cp	heat capacity [J/Kg.K
D_i	mass diffusion coefficient [m^2/s]
g	gravity [m/s^2]
h_i	latent heat of vaporization [J/Kg]
$k_{r,i}$	relative permeability
K	total permeability [m^2]
M_i, MM_i	molecular weight [Kg/mol]
$\dot{m}$	mass exchange between phases [$Kg/m^3.s$]
P	pressure [Pa]
r, R	radius [m]
R_g	perfect gases constant [$Pa.m^3/mol.K$]
Re	Reynolds number
S_{ring}	surface of one Pendular Ring (liquid-gas interface) [m^2]
S_i	phase saturation inorous media
Sc	Schmidt number
t	time [s]
T	temperature [K]
U_g	Darcy-speed of gas [m/s]
V	volume [m^3]
y	compound mass fraction in the gas phase

Greek letters

λ	thermal conductivity [W/m.K].
ρ	density [Kg/m^3].
ε	effective porosity of porous media
μ	dynamic viscosity [Kg/m.s]
φ	angle [rd]

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