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MODEL OF AROMATIC HYDROCARBONS TRANSPORT IN POROUS GROUND MEDIA

MODEL TRANSPORTU WĘGLOWODORÓW ROPOPOCHODNYCH W GRUNCIE POROWATYM

Abstract: Dispersion model of NAPL hydrocarbons' transport in porous media has been presented. Mathematical model allows to estimate whether the menace of ground water can occur as a result of hydrocarbons' transport through the soil. The convection in mass transport is considered in the general equation due to the higher velocity of propagation in vertical direction. The introduction of the equation of biosorption link allows to take into account microorganisms' influence on impurities concentration, especially on heavy oils derived compounds. The research conducted on a filter model was the first step to verify the dispersion model of petroleum derived substances. Dispersion coefficient was assessed for benzene, toluene and ethylbenzene.

Keywords: hydrocarbons, benzene, toluene , ethylbenzene, transport in soil

Industry development stimulates the growth of request for products derived from rock oil. Different kinds of substances of varied constitution are included in rock oil products:

- aliphatic and ramified chain structure
- aromatics and alicyclic hydrocarbons.

Prevalence of these products is the source of threat to the environment. The contamination of water and soil with organic substances derived from rock oil is one of the most important problems of present times [1]. Transport and degradation processes are important areas in the environment protection.

Recognition of these processes is a valid problem in environmental engineering as it is applied in technologies of waste treatment on landfills (leachates drained to the groundwater), transport of toxic substances from areas after ecological disaster in petrol stations, oil rock products stores, military traverse, etc.

During the flow of rock oil products through ground porous media processes of physical, chemical and biochemical nature take place. The transport, direction and promptness of distribution in porous matrix depend on the kind of contamination as well as on the structure and sorption ability of ground.

Rock oil derived substances introduced into the ground are initially driven in perpendicular direction by dispersion forces through ground aeration zone [2]. In the aeration zone some amounts of rock oil products are absorbed by rock particles while other amounts filter into the ground and often reach the groundwater mirror.

Transport of organic substances was analysed by several authors [3-8], but the problem of its mathematical description has been pointed out recently. Thus, in this aspect the phenomenon has not been properly recognised yet. However, it should be noted that a significant contribution in this field has been made by Parker [7].

Some writings can also be found in Polish literature, for example in [1] the mathematical model of oil rock substance infiltration in the soil has been presented. This

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model, though, has not been verified in actual conditions. The authors of this paper verified a similar model [5] on laboratory stand simulating real ground conditions.

Material and methods

Analytical form of aromatic hydrocarbons transport model

Transport of rock oil derived substances not soluble in water depends mainly upon their density, viscosity and ability to surface moisturizing [10]. Some constituents of rock oil show certain solubility in water (Fig. 1). Relatively high solubility characterises aromatics including among others benzene, toluene and ethylbenzene, which are detrimental for a human being due to their cancerous activity.

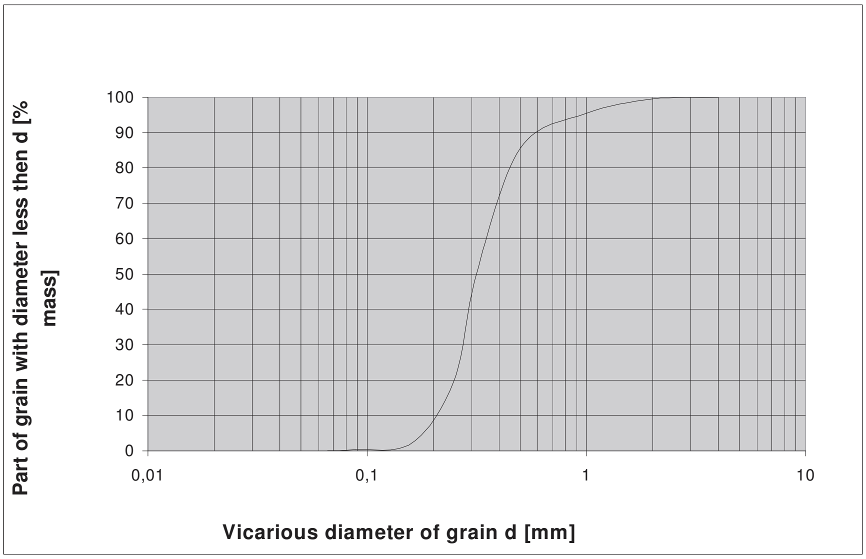

Fig. 1. Grain size distribution of primeval investigated sand

Benzene solubility in water is about 2600 times higher than octane solubility, but only 3.5 times higher than toluene solubility (Table 1).

Table 1

Solubility in water of chosen hydrocarbons (T = 298 K) [2]

Hydrocarbon	**Symbol**	**Solubility in water [g/m^3]**
n-pentane	C_5H_{12}	40.7
n-hexane	C_6H_{14}	9.5
n-octane	C_8H_{18}	0.68
cyclohexane	C_6H_{12}	55
benzene	C_6H_6	1780
toluene	C_7H_8	515
ethylbenzene	C_8H_{10}	310

Hydrocarbons detained in aeration zone can dissolve in rainwater and gradually infiltrate with it to the level of groundwater [2].

The aim of the authors' research was to suggest a theoretical model allowing to estimate the level of soil and ground water contamination after some specific time from the moment of soil surface contamination. It is also an element of risk estimation concerning groundwater contamination due to ecological disaster.

Tube reactor model applied to mass movement process

Let us now consider the fluid flow through a tube with constant diameter and accept conditions of a piston model flow. It means that every "slice" of liquid contained in the cylinder whose bases are sufficiently closely located in cross-section tube areas can be considered a special kind of unit system. That leads to the assumption that elements of velocity value or gradients of fluid of scalar quantity perpendicular to tube axis equal zero. However, axis gradients can exist. In non-stable condition mass balance of base constituent "i" can be formulated as follows:

Mass inflow to the system	-	Mass outflow from the system	-	Biosorption	=	Mass accumulation in the system

Taking hydrocarbons biosorption with soil microorganisms' activity into consideration we obtain a mathematical model described by the following formula:

$$\frac{\partial}{\partial y}\left(D_i \frac{\partial C_i}{\partial y}\right) - \frac{\partial (v \cdot C_i)}{\partial y} - k_i \cdot C_i = \frac{\partial C_i}{\partial t} \tag{1}$$

where: D_i - vicarious longitudinal coefficient of dispersion of key component "i" [m^2/s], C_i - "i" component concentration in a ground [kg/m^3], k_i - constant value of "i" component biosorption [1/s], t - time [s], y - impurities migration direction distance [m], ν - velocity of water flow thorough the ground matrix [m/s].

The stream dynamics consists of three elements: dispersion, convection, and biosorption, which are joined by one kinetic formula. Depending on the character of impurities migrating through porous ground matrix as well as on ground features, the influence of dispersion, convection and biosorption can vary to a large extent. To resolve the problem it is necessary to establish onset - and boundary conditions.

1. Onset condition:

a) $$C_i\,(y, 0) = 0 \quad \text{for} \quad 0 < y \le S \tag{2}$$

2. Boundary conditions:

a) $$C_i\,(0,t) = C_{i0} \cdot \exp(-k_i \cdot t) \quad \text{for} \quad t \ge 0 \tag{3}$$

b) $$\frac{\partial C_i}{\partial y} = 0 \quad \text{for} \quad t > 0 \quad \text{and} \quad y = S \tag{4}$$

where: S - the maximum depth of hydrocarbon penetration [m] through the ground, C_i - hydrocarbon concentration [kg/m^3], C_{i0} - initial hydrocarbon concentration [kg/m^3], t - time.

The run of the function $C_i = C_i(y,t)$, which is the solution of equation (1) is in most cases impossible to determine by analytical means. Thus, the numerical net methods (Crank-Nicolson method) can be used here, assuming that biosorption has only limited impact on migration of oil derived hydrocarbons [9] and the longitudinal dispersion coefficient is constant, the equation (1) can be expressed as follows:

$$\frac{\partial C_i}{\partial t} = D_i \frac{\partial^2 C_i}{\partial y^2} - \frac{\partial v C_i}{\partial y} - k_i \cdot C_i \tag{5}$$

The solution of equation (5) has a formula:

$$C_i(y,t) - \frac{C_{i0} \cdot S}{\sqrt{4 \cdot \pi \cdot D_i \cdot t}} \exp\left\{ - \left[\frac{(y - v \cdot t)^2}{4 \cdot D_i \cdot t} + k_i \cdot t \right] \right\} \tag{6}$$

Theoretical models took into account diffusive transportation of hydrocarbons and convection resulting from flow of water by aeration zone. Such models describe transport of hydrocarbons of stickinesses amounting to $\nu < 2 \cdot 10^{-6}\ m^2 \cdot s^{-1}$ efficiently.

The formula above (6) can be treated as an approximate solution of the boundary condition (5) limited by formulas (2), (3), (4). Formula (6) is applicable when time t refers to the migration of more than 95% of substance.

To simulate the real conditions the model of ground filter was constructed. It was column-shaped with a diameter of 190 mm and height of 1500 mm. The column was built from 15 cylinder-shaped segments, each 100 mm high. The column was filled with sand of selected grain size.

To research the migration of rock oil contaminations there were chosen three aromatic hydrocarbons:

- benzene
- toluene
- ethylbenzene.

Experimental researches were made with ground filter model filled with dry matrix in experimental conditions:

- ambient temperature t = (20 ± 0,5)°C,
- relative humidity of air (70 ± 2,5)%,
- atmospheric pressure 1013 hPa.

The function $C_i(y,t)$ finds numerous practical applications as it allows to estimate the real menace caused by migrating hydrocarbons in the porous ground.

Porosity ε ground NB. 1, 2 and 3 was signified in gauge cylinder of capacity 250 cm^3 where we measured 100 cm^3 of sampled hydrocarbons and we moved 200 cm^3 of grained material which have been previous boiled. After reading a measure of hydrocarbon in gauge cylinder (value a_w) we calculated porosity of matrix ε with reference to rock oil hydrocarbon using formula:

$$\varepsilon = \frac{(200 \div 100) - a_w}{200} \cdot 100\ [\%] \tag{7}$$

where a_w - measure of hydrocarbons in gauge cylinder [cm^3].

The analysis of the concentration distribution of hydrocarbons in a particular segment of the column allows to estimate the formal vicarious dispersion coefficient D_i in the system: sand - benzene, sand - toluene and sand - ethylbenzene by means of the model equation (6).

The research was carried out on sand media of the following parameters: porosity $\varepsilon = 0.32$, minimal grain diameter $d_{min.} = 0.5$ mm, maximum grain diameter $d_{max} = 2.0$ mm. The sand parameters were obtained by separation of sand (PN-98/B-04481) as presented in Figure 1 showing the grain distribution curve. The sand used in the experiment was dried at a temperature of 105°C to eliminate the transient moisture. There was no water transport in column ($\nu = 0$). The minimum biodegradation level of hydrocarbons' matter in ground was evaluated (k_i near zero). Investigations of hydrocarbons' matter migration velocity in different kinds of grounds were studied. The content of the matter in each segment of a column after hydrocarbons' exposition in time t, that is 1, 2, 4, 8 and 16 days respectively was determined.

A supplementary coefficient of hydrocarbons' diffusion was indicated by introducing the following quantities of the investigated hydrocarbon onto the top of the column to sandy matrix: 290, 145 or 72 kg/m^3 d.m.

Full cycle of investigations was repeated three times.

To signify a participation of rock oil hydrocarbon in ground matrix the method of gas chromatography with CS_2 extrahent was used. Content of aromatic hydrocarbons was determined with gas chromatograph type N-503 (2 m high sandy column filled with 5% SP-1200; 1,75 sentone 34).

The instrumental method applied to estimate total organic carbon is based upon a convenient and quick analysis of organic compounds dissolved in water. In this method carried out with IONICS 1505 IR apparatus was used to estimate hydrocarbons in water elutes (Fig. 2). The aforementioned device allows to determine TOC in the range from 1 to 1000 mg C/dm^3.

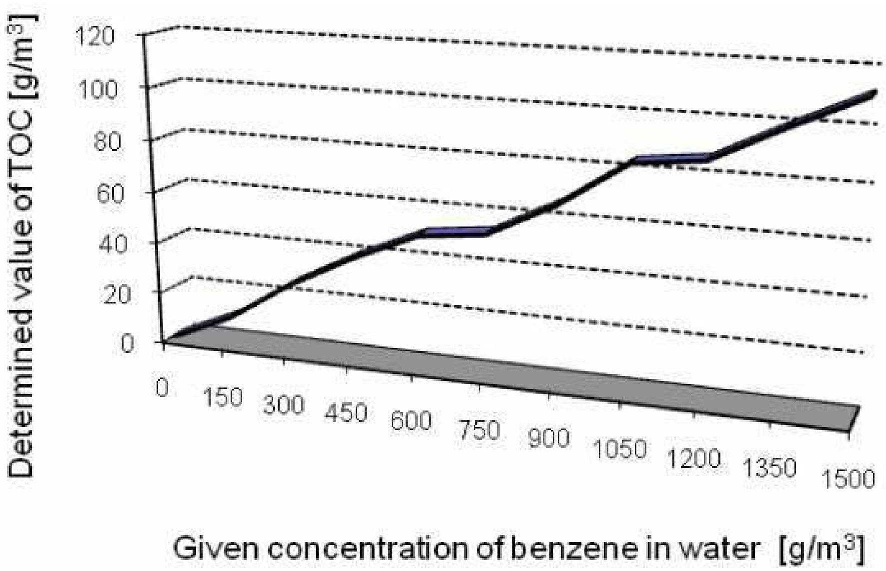

Fig. 2. The correlation of TOC and benzene concentration

The dispersion model is the analytical approach to hydrocarbons' migration process in porous media.

Results and discussion

The results concerning the hydrocarbons distribution in the column modelling the ground filter led to estimation of D_i parameter (Table 2). Example propagation velocity of hydrocarbons obtained base on ground filter model, was shown in Figure 3.

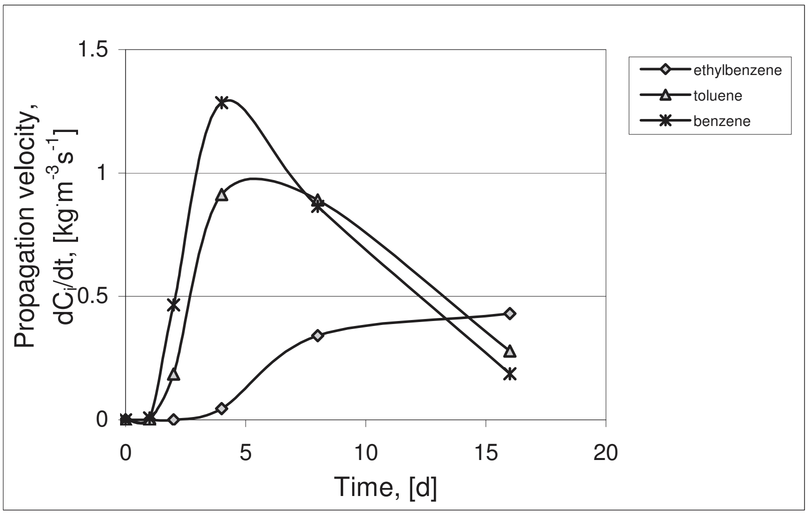

Fig. 3. Propagation velocity of hydrocarbons measured on the top of ground filter model

Table 2

Values of vicarious dispersion longitudinal coefficient determined on a ground model filter determined for $k_i = 0$ and $v = 0$

Hydrocarbon	**Dispersion coefficient D_i [m^2/s]**
Benzene	$9.81 \cdot 10^{-8}$
Toluene	$1.16 \cdot 10^{-7}$
Ethylbenzene	$1.32 \cdot 10^{-7}$

The laboratory results can be applied to real conditions of transport of hydrocarbons in the porous ground (half-defined area). Since the experiment was conducted on a sand filter with transient moisture eliminated by drying at 105°C, D_i values determined on sand bed can differ in practice, but they still allow to estimate the menace that exists in uncontrolled leakage of hydrocarbons including benzene and toluene.

In laboratory experiment the formal vicarious longitudinal dispersion coefficient D_i was determined in the system sand - benzene, sand - toluene and sand - ethylbenzene.

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MODEL TRANSPORTU WĘGLOWODORÓW ROPOPOCHODNYCH W GRUNCIE POROWATYM

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Abstrakt: W pracy wprowadzono dyspersyjno-konwekcyjny model migracji węglowodorów ropopochodnych w gruntach. Proponowany model jest próbą znalezienia mechanizmu propagacji węglowodorów przez ośrodek porowaty i pozwala przewidzieć, na ile migracja benzenu, toluenu i etylobenzenu jest w stanie zagrozić zwierciadłu wód podziemnych. Uwzględnienie konwekcji w równaniu transportu masy podyktowane jest zwiększoną szybkością migracji węglowodorów w kierunku pionowym. Wprowadzenie równania biosorpcji pozwala uwzględnić wpływ mikroorganizmów na zmianę stężenia, głównie ciężkich węglowodorów ropopochodnych w gruncie. Poprawność modelu zweryfikowano doświadczalnie na modelu filtra gruntowego poprzez wyznaczenie współczynnika dyspersji wzdłużnej dla benzenu, toluenu i etylobenzenu.

Słowa kluczowe: węglowodory ropopochodne, benzen, toluen, etylobenzen, transport w glebie