

Diffusion of lead ions through the Poznań Clay (Neogene) and through glacial clay

Radosław MIESZKOWSKI



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Two main kinds of migration through clays can be distinguished: advection and diffusion. The main force for advective flow is the water pressure gradient, while ionic concentration gradients drive diffusion. In compacted clays the hydraulic permeability is very low, therefore the diffusion process predominates. Clays can be considered as waste repositories. This paper shows characteristics of the diffusion process and the application of this process to modelling of waste migration in clays. Additionally, a new calculation method for the apparent diffusion coefficient using the finite-difference method is given. Experimental, values of the apparent diffusion coefficient D_{app} for Poznań Clay and glacial clay are respectively $2.2\pm 2.6 \times 10^{-12} \text{ m}^2/\text{s}$ and $2.6\pm 4.4 \times 10^{-12} \text{ m}^2/\text{s}$.

Radosław Mieszkowski, Faculty of Geology, University of Warsaw, PL-02-089 Warszawa, Al. Żwirki i Wigury 93; e-mail: mieszko@geo.uw.edu.pl (received: January 4, 2002; accepted: September 27, 2002).

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INTRODUCTION

Until recently only hydraulic conductivity has been considered in testing clay barriers planned for waste dumps, as this has been considered to be the most important parameter governing waste migration. However, research results (Shackelford, 1993) show that the rate of waste migration in saturated clays (at small hydraulic gradients) is determined mainly by molecular diffusion and not hydraulic conductivity. It is necessary, then, to analyse the diffusion of any solution (especially pollutants) in clays by:

- calculation of the diffusion parameter,
- realistic prediction of the process rate,
- mathematical diffusion modelling including additional conditions affecting the process.

This paper gives:

- a new method for calculating the apparent diffusion coefficient, which is easier to apply than previously published methods,
- examples of the use of this method, and comparisons of the results obtained with those derived using previously published methods.

In this paper it is assumed that the diffusion process can be described using Fick's Law. Justification for such an assumption

has been published: Lai and Martland (1960, 1961) indicated that the linear Fick's Law gives a good approximation of diffusion in bentonite clays. In this paper, beginning with Fick's assumption that the diffusion stream is proportional to the concentration gradient (Crank, 1979), a method is formulated to calculate the apparent diffusion coefficient. Furthermore, the experimental analysis is based on the assumption that the apparent diffusion coefficient is constant for saturated Poznań Clay, for glacial clay, and for selected diffusing substances.

DIFFUSION IN CLAYS

Diffusion through clays is slower than in free solution where there is no porous matrix. The apparent diffusion coefficient describes this diffusion. Many factors influence the coefficient value (Shackelford and Daniel, 1991a).

These authors produced equation [1] describing the factors influencing the apparent diffusion coefficient value:

$$D_{app} = \frac{D_{eff}}{R_d} \quad [1]$$

where: D_{eff} — effective diffusion coefficient [m^2/s]; R_d — retardation factor.

Table 1

Selected physical qualities of tested soils (NW)

Determinants	Poznań Clay	Glacial clay (author's experiments)
Name (PN-86/B-02480)	clay	clay
Age	Neogen	Warta Glaciation
Test depth [m]	6.0	1.0
Status	tpl	pl
Colour	Varicolored with light-brown areas	Brownish-yellow
Grain size	$f_p = 4\%$ $f_\pi = 26\%$ $f_i = 70\%$	$f_z = 2\%$ $f_p = 43\%$ $f_\pi = 20\%$ $f_i = 35\%$
Moisture content w [%]	30.6	27.5
Degree of saturated S_r	0.64	0.72
Specific gravity of solids [kN/m^3]	27.0	26.8
Bulk density γ [kN/m^3]	18.2	17.7
Porosity n	0.48	0.48
Voids ratio e	0.94	0.93

tpl — semi solid state; pl — plastic state; grain size: f_z — gravel, f_p — sand, f_π — silt, f_i — clay

The effective diffusion coefficient (D_{eff}) must be defined so as to consider this observation (Kemper *et al.*, 1964; Olsen and Kemper, 1968; Nye, 1979), equation [2]:

$$D_{eff} = D_0 \times \tau \times \alpha \times \gamma \times w \quad [2]$$

where: D_0 — free-solution diffusion coefficient of chemical species [m^2/s]; τ — tortuosity factor; α — fluidity or viscosity factor; γ — negative adsorption or anion exclusion factor; w — volumetric water content; for other explanations see equation [1].

Shackelford and Daniel (1991a) gave some of the factors affecting the determination of D_0 , τ , α , γ and w , as well some of their typical published values.

Solutes (of lead) that face any attenuation process in the soil are called “reactive solutes” (Leite *et al.*, 1998). A great number of reactions can take place when chemical species are in contact with soils (e.g. physical adsorption, chemical adsorption and precipitation). The use of the general term **sorption** is recommended. This process can be described by a retardation factor, which can be expressed by the following equation:

$$R_d = 1 + \frac{\rho_d \times K_p}{n} \quad [3]$$

where: ρ_d — dry density [g/cm^3]; n — effective porosity; K_p — the partition coefficient [cm^3/g]; for other explanations see equation [1].

It is able to describe the solute partition:

$$K_p = \frac{\partial q}{\partial C_e} \quad [4]$$

where: q — the sorbed concentrations [mg/g]; C_e — equilibrium concentration [mg/dm^3].

A graphical plot of q versus C_e is named the “adsorption isotherm”. It is a common practice to determine the sorption isotherms through a laboratory “Batch Test” (Witzak, 1984).

The second Fick's Law is given by the following partition equation:

$$\frac{\partial C}{\partial t} = D_{app} \frac{\partial^2 C}{\partial x^2} \quad [5]$$

where: D_{app} — apparent diffusion coefficient [m^2/s]; C — solute concentration [mg/dm^3]; x — direction [m] — as a sample; t — time [s].

MATERIALS

SOILS

Analysis of the lead diffusion process was carried out for two clays, common in Warsaw area: the Warta Glaciation clays (Quaternary) and the Poznań Clay (Tertiary). These soils may be potentially used as sealing materials for waste dumps. Selected physical qualities are collated in the Table 1.

To determine the mineral content of clay fraction tested, two analyses were used X-ray and derivatographic.

X-ray analysis was conducted with the reflexive X-ray diffractometer DRON-2 (USSR production) with the DRONEK computer registry system. The description of that method is given by Kulesza-Wiewióra (1990).

Thermal analysis was conducted with the LABSYS™ TG-DTA/DSC, device produced by the French company SETARAM registering curves in relation to the Al_2O_3 content.

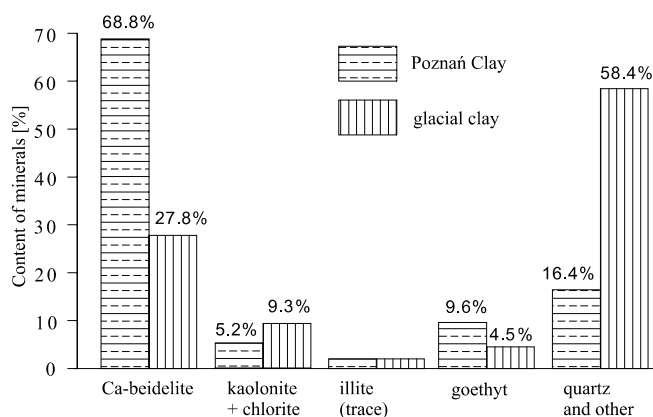


Fig. 1. Comparison of the mineral composition of the Poznań Clay and of glacial clay

The thermal analysis of clays is described by Wyrwicki (1996).

Both methods (Fig. 1) revealed a similar mineral content: the presence of smectite (beidelite), kaolinite and quartz. Furthermore, the X-ray analysis demonstrated small quantities of illite, which was not found in the thermal analysis. On the other hand, thermal analysis found traces of goethite and chlorite, not detected by X-ray analysis.

SOLUTIONS

Lead was selected as a diffusing substance due to its common presence in road areas and in industrial waste (coal and petroleum ashes). Additionally, the mobility of lead gives a good indication of the ability of the deposit to act as a barrier to harmful toxic pollutants (Kabata-Pendias and Pendias, 1993). In the experiments an aqueous solution of $\text{Pb}(\text{NO}_3)_2$ was used. Lead concentrations were as follows: 100, 250 and 500 mg/l (as in Roehl and Czurda, 1998). The pH reaction of all the solutions was between 6 and 7.

EXPERIMENTS

Diffusion of lead through sediments is slow, and so it is better to use mathematical modelling. As mentioned above the use Fick's Law for diffusion modelling in a deposit necessitates knowledge of the apparent diffusion coefficient. The coefficient value does not come directly from experiment, but is based on the measured concentration of the diffusing substance through concrete soil, at a given depth and specified time.

The value of the coefficient depends in part on the chemical concentration of the diffusing substance and in part on the soil type. Two methods of apparent diffusion coefficient calculation are presented below.

ADSORPTION ISOTHERMS

The retardation factor (R_d) was determined in a "Batch Test" for the following lead concentrations: 50, 100, 150, 200 and 250 mg(Pb)/dm³. Through the results of these experiments the nonlinear Freundlich isotherms were determined. The values of R_d for each concentration exceeded 1000. According to Witczak's scale (1984) the soils analysed could be characterised as possessing infinite sorption. Sorption has not been separately investigated in this study. The main subject of interest was the apparent diffusion coefficient, which described all the processes that influenced the rate of lead diffusion in clays.

METHODOLOGY

The first method of calculating the parameter has been previously published (e.g. Cho *et al.*, 1993). We could describe it as iterative (Fig. 2). The second finite difference method has been developed in this study.

Phase 1. The apparent diffusion coefficient (D_{app}) cannot be measured directly from experiments or under natural conditions. It is possible to measure the concentration ($C(x,t)$) of the

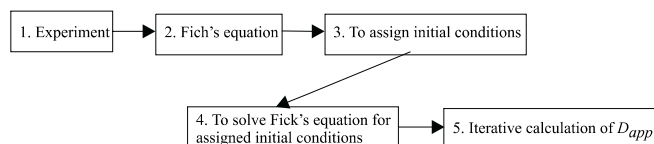


Fig. 2. The concept of the iterative method

diffusing substance in a specified period of time (t) from the moment when diffusion process begins and at a given distance from the diffusion source (x).

Phase 2. To calculate the apparent diffusion coefficient, the Fick's second Law is usually applied (equation [5]) in a one-dimensional case. It is a parabolic partial differential quadratic equation with a constant coefficient (D_{app}) describing only one-way (x) diffusion.

Phase 3. The solution of equation [5] depends on assigned initial and boundary conditions. The following assumptions were made:

- the sample where diffusion occurs is semi-infinite ($x \geq 0$);
- the concentration of diffusing ions at the point when the solution meets the sample is a constant (C_0);
- for depth going to infinity, concentration (C) goes to zero;
- it is presumed that at the beginning, when $t = 0$, the concentration of the substance in the sample equals zero.

Phase 4. Fick's equation is solved below with consideration of the above conditions.

$$C(x, t) = C_0 \times \left[1 - \frac{2}{\sqrt{\pi}} \sum_{n=0}^{\infty} (-1)^n \frac{\left(\frac{x}{\sqrt{4D_{app} \times t}} \right)^{2n+1}}{n!(2n+1)} \right] \quad [6]$$

where: C_0 — initial solute concentration [mg/dm³]; n — integer number; for other explanations see equation [5].

Phase 5. To calculate D_{app} , we can use the iterative method substituting the value until the left side of the equation [6] equals the right side. It is difficult, because the unknown is within the set of numbers from 1 to ∞ .

The new idea how to calculate the apparent diffusion coefficient, developed here, uses the finite differences method.

Its application does not require complex mathematical and numerical calculations, which makes it very effective. In this method (Fig. 3) the research starts by testing 3 samples of the same soil, with the same humidity and volume weight. It is the essence of the experiment. Prepared samples are put into the diffusion chambers and flooded with a solution of the same initial concentration (C_0) (indexing ions). After a declared time ($t - \Delta t$) the test of one sample is finished and the concentration of the diffusing substance in the sample is marked (C) at depth (x). The selected depth (x) can be neither at the top nor the bottom of the sample. After a few days (time Δt) diffusion in the second sample is stopped. Likewise, the concentration (C) is

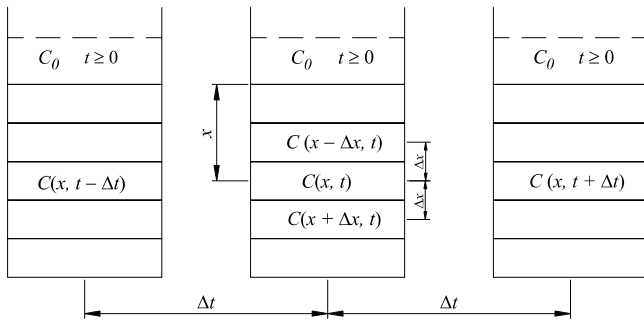


Fig. 3. The scheme represents the concentration measurement of diffusing ions

marked at depth (x) and two concentration values at depth ($x - \Delta x$) and ($x + \Delta x$). Next, the diffusion of third sample is stopped after the time ($t + \Delta t$) and is marked with concentration (C) at depth (x).

The results allow determination of the apparent diffusion coefficient straight from the transformed equation [5].

$$D_{app} = \frac{\frac{\partial C}{\partial t}}{\frac{\partial^2 C}{\partial x^2}} \quad [7]$$

for explanations see equation [5].

Correspondingly, applying the finite difference method we can rewrite it as follows (e.g. Farlow, 1982):

$$\frac{\partial^2 C(x, t)}{\partial x^2} \approx [C(x + \Delta x, t) - 2C(x, t) + C(x - \Delta x, t)] \times \frac{1}{(\Delta x)^2} \quad [8]$$

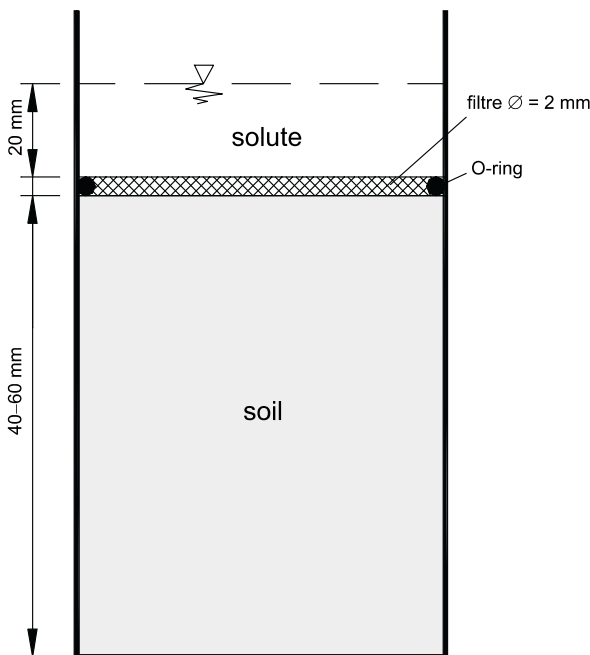


Fig. 4. Diagram of the diffusion cell

$$\frac{\partial C}{\partial t} \approx [C(x, t + \Delta t) - C(x, t - \Delta t)] \times \frac{1}{2\Delta t} \quad [9]$$

for explanation of the symbols from equation [8] and [9] see Figure 3.

EXPERIMENT

The diffusion experiment was conducted in cells (Fig. 4), specially designed for this purpose. In the cells, the index solution (placed on the top of the sample) had been diffusing with lead ions. Diffusion took place through thick and water-saturated soil samples (Poznań and glacial clays), under the

Table 2

Selected physical qualities of the soils after consolidation

Determinants	Poznań Clay	Glacial clay
Bulk density γ [kN/m ³]	15.4	17.1
Moisture content w [%]	74.0	42.9
Degree of saturated S_r	1.01	0.93
Porosity n	0.69	0.56
Voids ratio e	2.25	1.26

influence of the concentration gradient of migrating ions.

To calculate the apparent diffusion coefficient, laboratory testing was carried out of 10 samples of Poznań Clay and 10 of glacial clay. From the samples, soil pastes were prepared and consolidated. Selected physical qualities of the soils after consolidation are listed in Table 2.

The experiment regarding proposed concentrations of the lead solutions took 30, 60 and 90 days. After corresponding times the diffusion process was interrupted in each chamber. Each sample after removal from a particular chamber was cut into 5 mm slices (Fig. 5).

The middle parts of the slices were selected to determine the concentrations of diffusing ions, to prevent the possible influence of solutions migrating along chamber walls. The con-

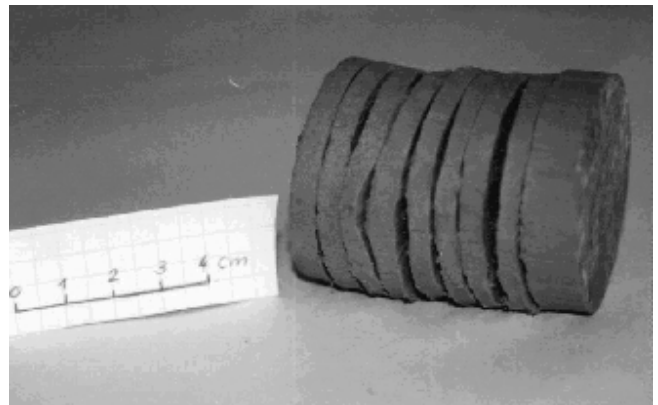


Fig. 5. The sample of glacial clay prepared to determine the concentration of lead

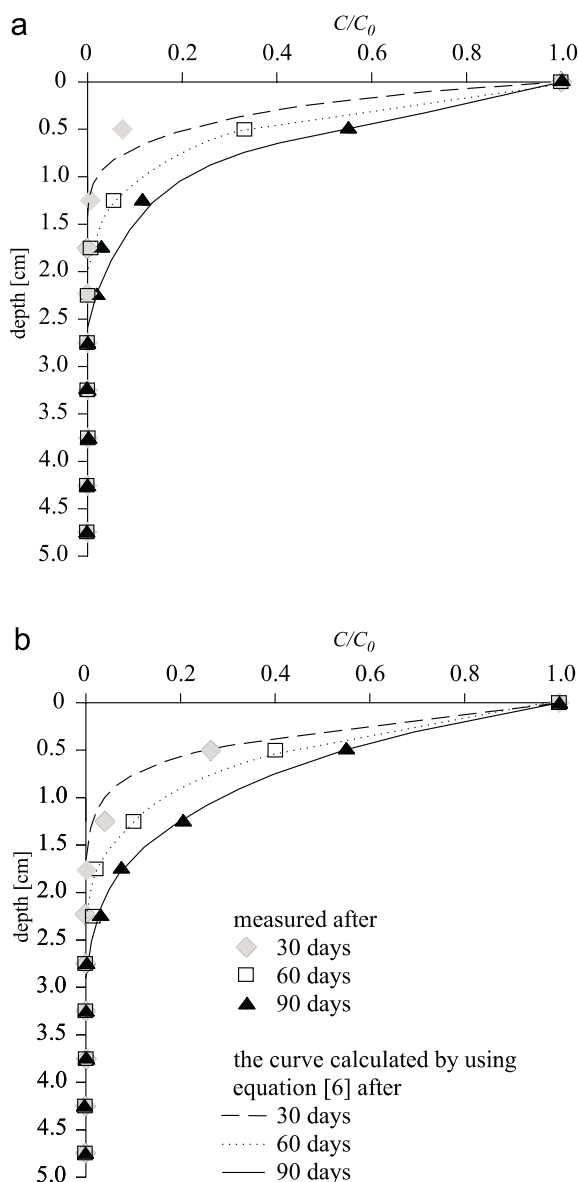


Fig. 6. **a** — distribution of diffusing lead ions in Poznań Clay samples, $C_0 = 500$ mg/l; **b** — distribution of diffusing lead ions in glacial clay samples, $C_0 = 500$ mg/l

centration of lead was determined in soils using the measuring device spectrophotometer *FAAS*. The methodology is described in Tessier *et al.* (1979).

Figures 6a and b shows an example of the distribution of diffusing lead ions in the tested soils.

In the graphs (Fig. 6a and b), horizontal axis describes the ratio of measured lead ion concentration (C) in samples (in relation to time (t) and depth (h)) to the initial concentration of index solutions (C_0) (respectively 100, 250, 500 mg/l). Theoretical curves describing the distribution of concentrations in the diffusing solutions (marked on Fig. 6a and b with continuous lines) were determined from modified equation [6]:

$$\frac{C(x, t)}{C_0} = \left[\operatorname{erfc} \left(\frac{x}{\sqrt{4D_{app} \times t}} \right) \right] \quad [10]$$

where: $\operatorname{erfc}(z) = 1 - \operatorname{erf}(z)$, ($\operatorname{erf}(z)$ — error function); x — depth; for other explanations see equation [6].

From laboratory determinations of the distribution of ionic concentrations (points marked on Fig. 6a and b), for all tests, the diffusion value was calculated iteratively from equation [10]. Next, the average values of apparent diffusion coefficients, relative to a given group of initial concentration values C_0 (500 mg/l) and to the time of experiment (30, 60 and 90 days), were substituted in the equation [10].

RESULTS

To calculate the apparent diffusion coefficient values in the tested soils (Poznań Clay and Warta Glaciation clays) it was necessary to know:

- the distribution of concentration of diffusing lead ions $C(x, t)$ (mg/dm³);
- initial concentration values of the diffusing solutions C_0 (mg/dm³);
- the timeframe of the diffusion process (experiment) t (s);
- the depth at which the concentration of diffusing lead ions was determined x (m).

The values of apparent diffusion coefficients were calculated in two ways:

- iterative, using prepared solutions of Fick's equation [10] for assigned initial and boundary conditions;
- the technique outlined in this paper, using the finite differences method.

USING THE ITERATIVE METHOD TO CALCULATE THE APPARENT DIFFUSION COEFFICIENT

To calculate the apparent diffusion coefficient value, a solution of Fick's [6] equation was selected for earlier described initial and boundary conditions. In that equation [6] only the apparent diffusion coefficient value D_{app} is unknown, all remaining values being recognised. The iterative calculations were done by the licensed program *MS EXCEL 97*.

THE NEW METHOD OF CALCULATING THE APPARENT DIFFUSION COEFFICIENT

The value of the apparent diffusion coefficient was calculated using equations [8] and [9] for measured concentrations $C(x - \Delta x, t)$, $C(x, t)$, $C(x + \Delta x, t)$, $C(x, t - \Delta t)$ and $C(x, t + \Delta t)$ (Fig. 3). The following assumptions were made: Δx — the difference in distance between two slices of soil samples (0.5 cm); t — time of the experiment (30, 60 and 90 days); Δt — period of experiment interruption (every 30 days).

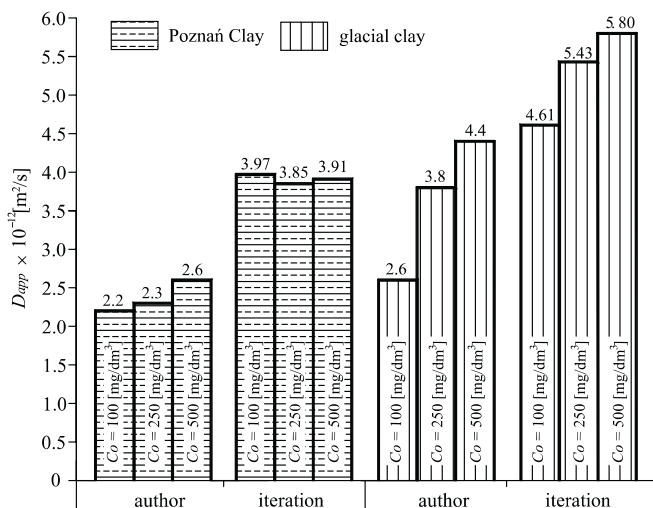


Fig. 7. Comparison of coefficient D_{app} value determined with the two methods

EXAMPLE

A calculation method for the apparent diffusion coefficient in Poznań Clay, at index solution concentration equal to 100 mg/dm^3 , is given below:

$C(x, t - \Delta t) = 0.01 \text{ mg/dm}^3$ concentration of lead ions at depth $x = 1.75 \text{ cm}$ after time 30 days;

$C(x, t) = 0.17 \text{ mg/dm}^3$ concentration of lead ions at depth $x = 1.75 \text{ cm}$ after time 60 days;

$C(x, t + \Delta t) = 3.44 \text{ mg/dm}^3$ concentration of lead ions at depth $x = 1.75 \text{ cm}$ after time 90 days;

$C(x - \Delta x, t) = 7.89 \text{ mg/dm}^3$ concentration of lead ions at depth $x = 1.25 \text{ cm}$ after time 60 days;

$C(x + \Delta x, t) = 0.01 \text{ mg/dm}^3$ concentration of lead ions at depth $x = 2.25 \text{ cm}$ after time 60 days;

$\Delta x = 0.005 \text{ m}$

$\Delta t = 30 \text{ days} = 2592000 \text{ s}$.

$$\frac{\partial^2 C(x, t)}{\partial x^2} = [0.01 - 2 \times 0.17 + 7.89] \times \frac{1}{(0.005)^2} =$$

$$= 302400 \frac{\text{mg}}{\text{dm}^3} \times \frac{1}{\text{m}^2}$$

$$\frac{\partial C}{\partial t} = \frac{1}{2 \times 2592000} \times [3.44 - 0.01] = 6.61651 \times 10^{-7} \frac{\text{mg}}{\text{dm}^3} \times \frac{1}{\text{s}}$$

The results of the above calculation are substituted into equation [7] and as a result we can obtain the value of apparent diffusion coefficient.

$$D_{app} = \frac{\frac{\partial C}{\partial t}}{\frac{\partial^2 C}{\partial x^2}} = \frac{6.61651 \times 10^{-7}}{302400} = 2.2 \times 10^{-12} \frac{\text{m}^2}{\text{s}}$$

The value represents the average apparent diffusion coefficient for a given research area; meaning the three soil samples through which the solution of equal initial concentration diffused. The remaining values of apparent diffusion coefficient were calculated in the same manner. The results are collected in Figure 7.

In Table 3 the values of apparent diffusion coefficients obtained in this study are compared with published data.

CONCLUSIONS

The two methods gave different values for the apparent diffusion coefficients. In the Poznań Clay samples, the difference in the values are in the range of 33–44%. The method of apparent diffusion coefficient calculation obtained here is approximated, based on numerical finite difference method.

The finite difference method gives more exact results when Δt and Δx obtain values close to zero. Such a relatively great

Table 3

The comparison of apparent diffusion coefficients

Source	Soil	$\text{Cd}^{2+} \times 10^{-12} [m^2/s]$	$\text{Pb}^{2+} \times 10^{-12} [m^2/s]$	$\text{Zn}^{2+} \times 10^{-12} [m^2/s]$	$\text{K}^+ \times 10^{-12} [m^2/s]$	$\text{Na}^+ \times 10^{-12} [m^2/s]$
Roehl and Czurda (1998)	clay	4.9÷6.7	0.36÷0.74	–	–	–
Leite <i>et al.</i> (1998)	clay	–	–	–	918÷3480	–
Shackelford and Daniel (1991b)	kaolinite clay	200	–	131	–	–
	smektite clay	36	–	127	–	–
Crooks and Quigley (1984)	clay	–	–	–	–	250
Mieszkowski	clay (Poznań Clay)	–	2.2÷2.6	–	–	–
	clay (glacial clay)	–	2.6÷4.4	–	–	–

difference in the calculated apparent diffusion coefficients could be justified by the time partition $\Delta t = 30$ days and distance $\Delta x = 0.5$ cm. If those values were smaller, the spread in D_{app} values between both methods may decrease.

Both methods give approximate values of the apparent diffusion coefficient (D_{app}). In the iterative method some assumptions are not consistent with experimental results and may lead to inconsistencies:

— the assumption that the sample is infinitely long and that the concentration decreases with depth to infinity. In experi-

ments the sample had a finite length and after a certain time of diffusion, the result can be wrecked by the lower boundary of the sample, which was isolated.

— the assumption, that calculation of equation [6] in the iterative method can be misleading due to numerical problems. The concentration, represented by equation [6] portrays the equation, in which the right side is an infinite series. For analytical purposes only 100 series terms were used, and this may introduce errors.

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