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## APPLICATION OF POLLUTE<sub>v.6</sub> PROGRAM IN THE INTERPRETATION OF CONTAMINANT TRANSPORT IN PRB

*Received: 25 January 2008*

*Accepted: 20 October 2008*

High chemical concentration of contaminants in aquifers, with reached or exceeded threshold trigger values, can have negative effects on ecological systems and is liable to cause hazards to human health. Permeable reactive barriers (PRB) represent a promising technology for groundwater protection. The zeolite-sand mixture is proposed as a reactive material filling PRB in the neighborhood of municipal and industrial waste disposal sites. To understand the processes which occur during the contact of reactive materials and polluted groundwater, in situ and laboratory tests are usually recommended. The tests of contaminant migration through the attenuation zone can be interpreted using the POLLUTE<sub>v.6</sub> program, which solves one-dimensional advection-dispersion equation. In this study hydraulic (Darcy velocity and dispersion coefficient) and sorption parameters (partitioning coefficient) were determined for zeolite-sand mixtures.

Key words: contaminants migration, zeolite-sand mixture, breakthrough curves

### 1. INTRODUCTION

In recent years a number of technologies has been developed for groundwater remediation. The most promising technology of purifying beds

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in-situ saturated with water is the application of a permeable reactive barrier (PRB) (Fig. 1). This method includes the performance of a continuous wall or funnel-and-gate systems situated across the flow paths of polluted groundwater [1]. Due to this, it is possible to remove the pollutants without extracting the contaminated soils and water to the ground surface. After passing the polluted groundwater through a barrier filled with a reactive medium, the contaminants are transformed into less hazardous substances or are attached to the medium through physical or chemical sorption. Therefore, it is important to find a cost-effective adsorbent for universal application in the PRB. The concept of adsorption of inorganic compounds (heavy metals, ammonium) on zeolites is not new and is widely applied in water treatment [2, 3, 4, 5, 6, 7] and landfills construction [8]. Recently, in order to prove the advantages of zeolite-sand mixtures as sorbents fulfilled the attenuation zone of the PRBs comprehensive investigations have been undertaken at the Department of Geotechnical Engineering at WULS (Warsaw University of Life Sciences) [9,10].

The aim of this work is focused on the contaminant transport mechanisms through samples of zeolite-sand mixtures and thereafter on the mathematical treatment of the experimental data in order to determine the relations governing a sorption barrier. Back analysis (“trial and error” procedure) using the numerical POLLUTEv.6 program [11] was applied to estimate the unknown sorption parameters of zeolite-sand mixtures.

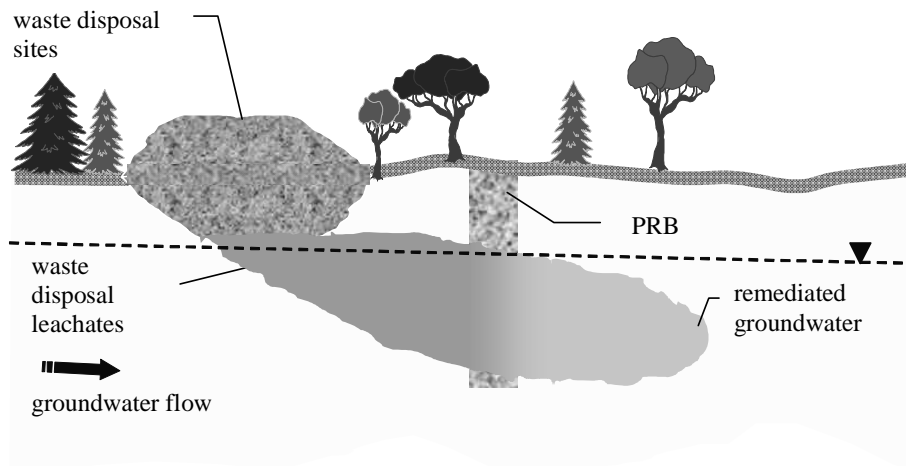


Fig. 1. Operating scheme of a PRB

## 2. DESCRIPTION OF THE POLLUTEv.6 PROGRAM

POLLUTEv.6 is one of the widely used numerical programs modeling contaminant migration from landfills. A contaminant transport model consists of the governing equation together with the boundary and initial conditions. Using the finite-layer formula the program calculates the concentration of contaminants at defined time steps and depths. The contaminant concentration can be directly obtained at any defined time without calculating the concentration at earlier time steps [12]. The finite layer technique is applicable solely to cases when the system can be idealized as being horizontally layered, with the soil parameters being the same at any horizontal location within the layer. The POLLUTEv.6 program is easy to use; the user may not be an expert in numerical analysis. Furthermore, the program requires minimum input and gives the results for selected time steps and locations.

The numerical description of dissolved contaminant migration through porous materials is based on the knowledge of transport mechanisms such as filtration (advection, diffusion and dispersion) and retardation (sorption, precipitation, chemical and biological decay). These mechanisms have been widely described in literature [12, 13].

In the POLLUTEv.6 program, contaminant migration in one dimension in an intact material is governed by the equation

$$n \frac{\partial c}{\partial t} = nD \frac{\partial^2 c}{\partial z^2} - nv \frac{\partial c}{\partial z} - \rho K_d \frac{\partial c}{\partial t} - \lambda c, \quad (2.1)$$

where:

- $c$  – concentration of contaminant at depth  $z$  at time  $t$  [ $\text{mg}/\text{dm}^3$ ],
- $D$  – coefficient of hydrodynamic dispersion at depth  $z$  [ $\text{m}^2/\text{s}$ ],
- $v$  – groundwater velocity at depth  $z$  [ $\text{m}/\text{s}$ ],
- $n$  – porosity of soil at depth  $z$  [-],
- $\rho$  – dry density of soil at depth  $z$  [ $\text{kg}/\text{m}^3$ ],
- $K_d$  – partitioning (sorption) coefficient at depth  $z$  [ $\text{m}^3/\text{kg}$ ],
- $\lambda$  – decay constant of contaminant species [ $\text{d}^{-1}$ ].

This relationship (2.1) results from the mass conservation law and the assumption that the concentration of contaminants that increased in the reference soil volume is equal to the increase of mass transported due to advection and diffusion minus the mass that was retarded. This equation is solved using the boundary conditions at the top and bottom of the soil sample being modeled. In the POLLUTEv.6 program there are three boundary conditions at the top of the sample: zero flux, constant concentration and finite mass, and four at bottom: zero flux, constant concentration, fixed outflow and infinite thickness [11].

In this paper sorption is considered as the retardation mechanism, whereas other processes that could take place were not taken into consideration. Sorption is the process during which contaminants are removed from the solution by fixation on solid matter in soil. Typical interactions include cation exchange of inorganic compounds on the zeolite surface. Sorption is usually modeled as a function of the contaminant concentration in the soil. The POLLUTEv.6 program uses three models that typically describe this process in soils: linear sorption, Freundlich non-linear sorption and Langmuir non-linear sorption. The linear approximation is valid for low concentrations of contaminants, whereas sorption generally is non-linear for high concentrations [12]. When non-linear sorption is assumed, POLLUTEv.6 splits the soil sample into sublayers and an iterative technique is applied to determine equivalent linear distribution coefficient ( $K_d$ ) values for each layer. The Freundlich non-linear sorption is represented by the relationship

$$S = K_f c^\varepsilon, \quad (2.2)$$

where:  $S$  – mass of the solute sorbed per unit mass of soil [mg/g],  
 $K_f$  – an empirically determined parameter [ $\text{dm}^3/\text{g}$ ],  
 $\varepsilon$  – an empirically determined exponent [-].

and the Langmuir non-linear sorption is expressed by the equation

$$S = \frac{S_m bc}{1 + bc}, \quad (2.3)$$

where:  $S$  – mass of the solute sorbed per unit mass of soil [mg/g],  
 $S_m$  – solid phase concentration corresponding to all available sorption sites being occupied [mg/g],  
 $b$  – a parameter representing the rate of sorption [ $\text{dm}^3/\text{g}$ ],  
 $c$  – a concentration of the solute [ $\text{mg}/\text{dm}^3$ ].

According to Rowe [11], the empirical parameters of these two models ( $K_f$ ,  $\varepsilon$ ,  $S_m$  and  $b$ ) are best determined by performing batch tests on the samples. It should be emphasized that the values of these parameters estimated from the batch tests can differ compared to dynamic tests. Nevertheless, in this study the results of the batch tests have been applied as initial values to model contaminant transport through the zeolite-sand samples.

### 3. MATERIALS AND METHODS

#### 3.1. Materials

Tests, completely new in the research domain, were carried out on clinoptilolite-rich Slovak zeolite tuff (from the Nižny Hrabovec deposit) (SZ) in a granular form with particle sizes of 1.0 to 2.5 mm and on zeolite-sand mixtures (with 20%, 50% content of zeolite in the mixture). The applied sand was from the Vistula deposit near Warsaw (medium sand). Grain size distributions of the materials used are presented in Fig 2. Prior to laboratory column tests, the homo-ionic form of SZ was prepared by the treatment with sodium chloride solution. The zeolite samples were shaken with 5% NaCl for 24 h and washed with distilled water until all  $\text{Cl}^-$  was removed, then dried at 105 °C and stabilized in air temperature.

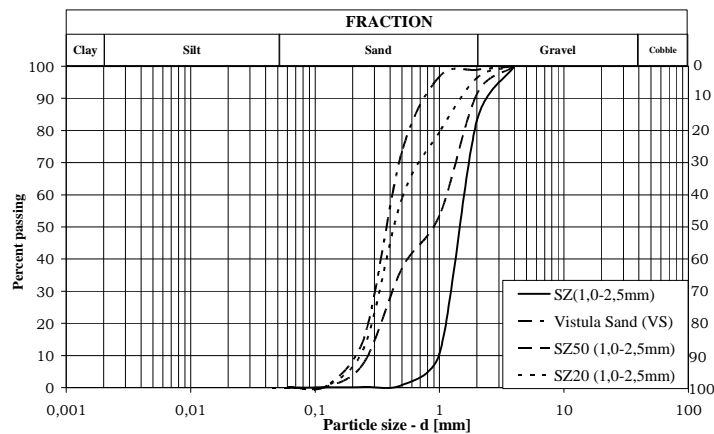


Fig. 2. Grain size distribution of zeolite, sand and zeolite-sand mixtures

#### 3.2. Column tests

Experiments in columns were designed to be representative for the field conditions. Dynamic flow experiments were performed using three PVC columns, 0.80 m-long and of 0.99 m internal diameter (Fig. 3). In order to assure the optimal flow distribution in columns quartz sand filters were placed at each end of the columns. The inflow concentrations were measured at the border between the quartz filter and the zeolite-sand mixture. Properties of the materials tested in the columns are shown in Table 1. The flow rates through the columns were adjusted to simulate real rates in the aquifer, in order to reproduce the behavior of the barrier and the pollutants in the field conditions.

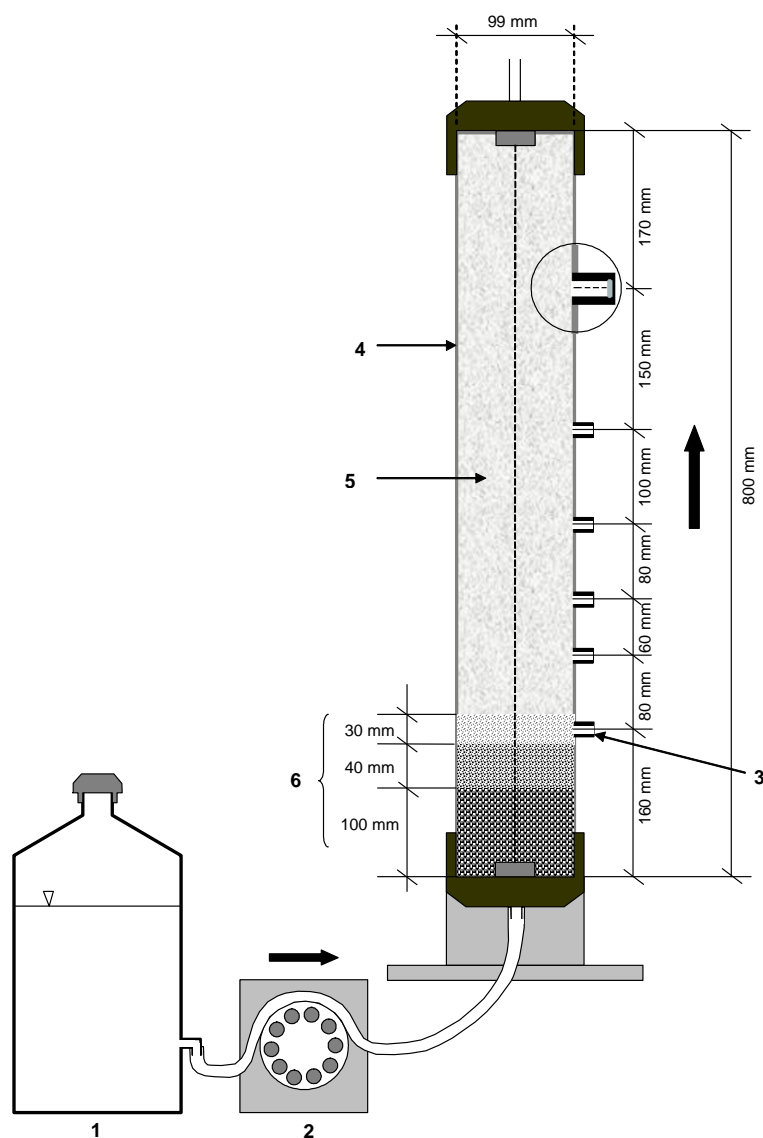


Fig. 3. Schematics of the column test equipment: 1 – tracer reservoir, 2 – peristaltic pump,  
3 – sample port, 4 – PVC column, 5 – reactive material, 6 – quartz filter

A multichannel peristaltic pump (ISMATEC) was used to impose the solution flow through the columns (from bottom to the top) at a constant flow rate. The zeolite-sand mixtures were fed with metal- and ammonium-free

distilled water from bottom to the top of the columns. After estimating a steady flow rate of  $4.17 \cdot 10^{-8} \text{ m}^3/\text{s}$ , a slug input of the nonreactive tracer (chloride  $310 \text{ mg}/\text{dm}^3$  – columns Nos. 1 and 4) and the reactive tracer ( $\text{NH}_4^+$   $360 \text{ mg}/\text{dm}^3$  – column No. 2,  $\text{NH}_4^+$   $273 \text{ mg}/\text{dm}^3$  and  $\text{Cu}^{2+}$   $100 \text{ mg}/\text{dm}^3$  in the presence of  $\text{Ca}^{2+}$   $100 \text{ mg}/\text{dm}^3$  and  $\text{Mg}^{2+}$   $200 \text{ mg}/\text{dm}^3$  - columns Nos. 3 and 5) was added to evaluate the hydrodynamic characteristics and contaminants transport parameters for each column. The aqueous samples were periodically collected from the outlet and from the column ports and analyzed for  $\text{Cl}^-$ ,  $\text{NH}_4^+$ ,  $\text{Cu}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ , pH-values and electrical conductivity. The tests were finished at complete breakthrough (i.e. when the effluent concentration equaled that of the influent).

Table 1 Properties of the tested materials

Column No.	Mass of dry material [g]	Zeolite content [-]	Bulk density [ $\text{kg}/\text{m}^3$ ]	Porosity [-]	Effective porosity [-] <sup>1)</sup>	Column PV [ $\text{m}^3$ ]
1	8931,3	0.5	1440	0,42	0,36	$2.246 \cdot 10^{-3}$
2	6732.3	0.5	1440	0,42	0,36	$1.669 \cdot 10^{-3}$
3	6732.3	0.5	1440	0,42	0,36	$1.669 \cdot 10^{-3}$
4	10008.7g	0.2	1600	0,38	0,33	$2.039 \cdot 10^{-3}$
5	7433.3	0.2	1600	0,38	0,33	$1.530 \cdot 10^{-3}$

<sup>1)</sup> estimated by use of a non-reactive tracer (chloride)

#### 4. INTERPRETATION OF LABORATORY TESTS

The results of tests in the columns of zeolite-sand material are usually presented by breakthrough curves that illustrate the relationship between the solute outlet concentration versus time. In this study the outlet concentration is expressed as the absolute concentration of chemicals C.

In the numerical modeling the following boundary and initial conditions were assumed:

- top boundary - constant concentration of chosen ions in the influent solution

$$C(0,t) = C_0 \quad \text{dla } t \geq t_0, \quad (3.1)$$

- bottom boundary - infinite thickness,
- initial boundary - zero initial concentration in the sample

$$C(x,0) = 0 \quad \text{dla } x \geq 0. \quad (3.2)$$

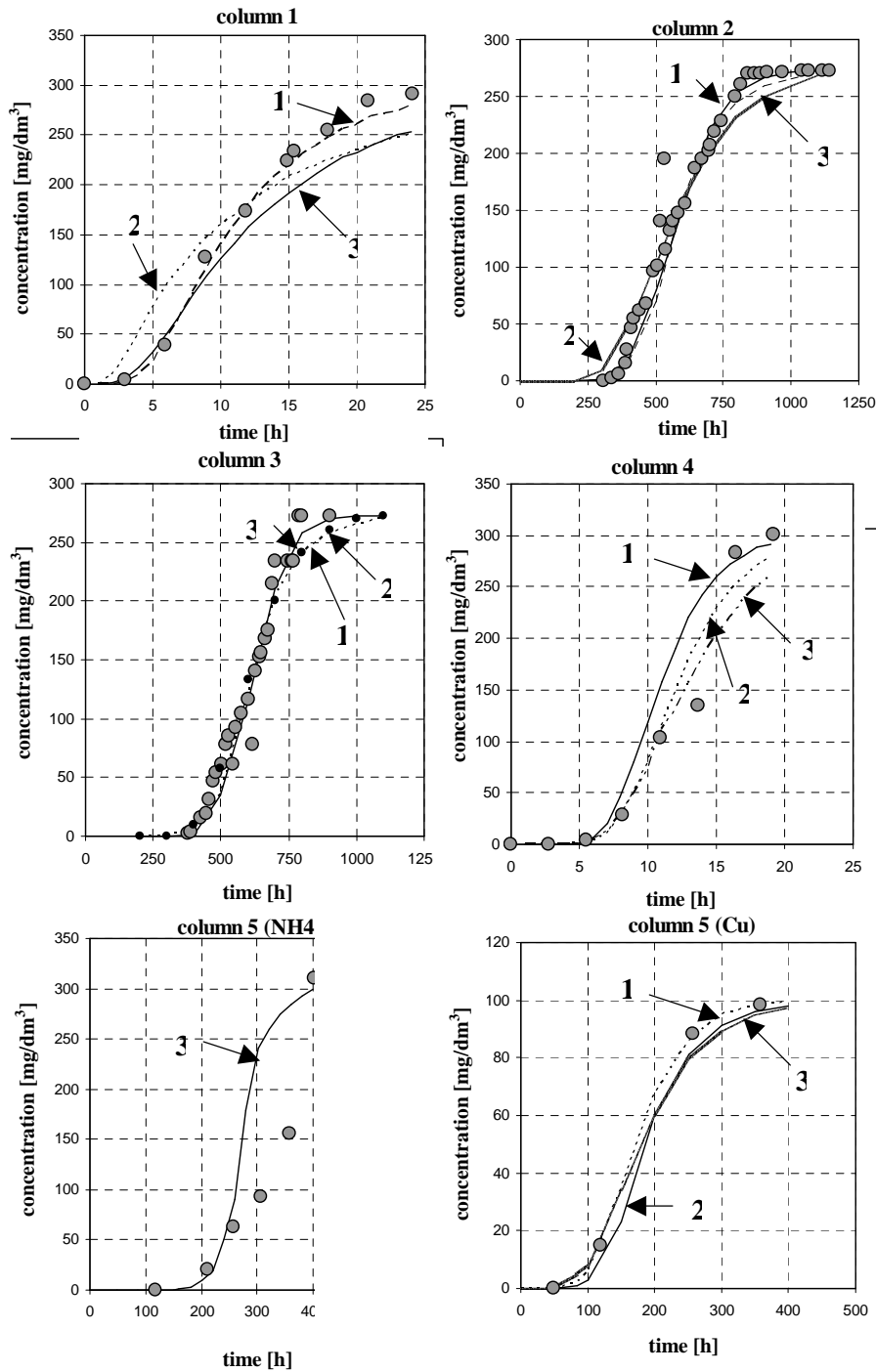


Fig. 4. Breakthrough curves for zeolite-sand mixtures

Table 2. Description of breakthrough curves shown in Fig. 4

	curve 1	curve 2	curve 3
<b>column 1</b>	$D = 2.5 \cdot 10^{-6} \text{ m}^2/\text{s}$ $v = 6.5 \cdot 10^{-6} \text{ m/s}$	$D = 7.5 \cdot 10^{-6} \text{ m}^2/\text{s}$ $v = 5.41 \cdot 10^{-6} \text{ m/s}$	$D = 3.5 \cdot 10^{-6} \text{ m}^2/\text{s}$ $v = 5.41 \cdot 10^{-6} \text{ m/s}$
<b>column 2</b>	<u>Linear model</u> $D = 3.0 \cdot 10^{-7} \text{ m}^2/\text{s}$ $v = 6.5 \cdot 10^{-6} \text{ m/s}$ $K_d = 1.55 \cdot 10^{-2} \text{ m}^3/\text{kg}$	<u>Langmuir model</u> $D = 7.0 \cdot 10^{-7} \text{ m}^2/\text{s}$ $v = 6.5 \cdot 10^{-6} \text{ m/s}$ $S_m = 55 \text{ mg/g}$ $b = 0.4 \text{ dm}^3/\text{g}$	<u>Freundlich model</u> $D = 9.0 \cdot 10^{-7} \text{ m}^2/\text{s}$ $v = 6.5 \cdot 10^{-6} \text{ m/s}$ $K_f = 800 \text{ dm}^3/\text{g}$ $\varepsilon = 0.27$
<b>column 3</b>	<u>Linear model</u> $D = 3.0 \cdot 10^{-7} \text{ m}^2/\text{s}$ $v = 6.5 \cdot 10^{-6} \text{ m/s}$ $K_d = 1.65 \cdot 10^{-2} \text{ m}^3/\text{kg}$	<u>Langmuir model</u> $D = 1.5 \cdot 10^{-7} \text{ m}^2/\text{s}$ $v = 6.5 \cdot 10^{-6} \text{ m/s}$ $S_m = 50 \text{ mg/g}$ $b = 0.5 \text{ dm}^3/\text{g}$	<u>Freundlich model</u> $D = 7.0 \cdot 10^{-7} \text{ m}^2/\text{s}$ $v = 6.5 \cdot 10^{-6} \text{ m/s}$ $K_f = 720 \text{ dm}^3/\text{g}$ $\varepsilon = 0.3$
<b>column 4</b>	$D = 7.0 \cdot 10^{-7} \text{ m}^2/\text{s}$ $v = 6.5 \cdot 10^{-6} \text{ m/s}$	$D = 7.0 \cdot 10^{-7} \text{ m}^2/\text{s}$ $v = 5.8 \cdot 10^{-6} \text{ m/s}$	$D = 8.5 \cdot 10^{-7} \text{ m}^2/\text{s}$ $v = 5.41 \cdot 10^{-6} \text{ m/s}$
<b>column 5 (Cu)</b>	<u>Linear model</u> $D = 7.0 \cdot 10^{-7} \text{ m}^2/\text{s}$ $v = 5.8 \cdot 10^{-6} \text{ m/s}$ $K_d = 3.5 \cdot 10^{-3} \text{ m}^3/\text{kg}$	<u>Langmuir model</u> $D = 1.0 \cdot 10^{-6} \text{ m}^2/\text{s}$ $v = 5.41 \cdot 10^{-6} \text{ m/s}$ $S_m = 21 \text{ mg/g}$ $b = 0,2 \text{ dm}^3/\text{g}$	<u>Freundlich model</u> $D = 1.5 \cdot 10^{-6} \text{ m}^2/\text{s}$ $v = 5.8 \cdot 10^{-6} \text{ m/s}$ $K_f = 140 \text{ dm}^3/\text{g}$ $\varepsilon = 0.18$
<b>column 5 (NH<sup>4+</sup>)</b>	-	-	<u>Freundlich model</u> $D = 8.5 \cdot 10^{-7} \text{ m}^2/\text{s}$ $v = 6.5 \cdot 10^{-6} \text{ m/s}$ $K_f = 1500 \text{ dm}^3/\text{g}$ $\varepsilon = -6 \cdot 10^{-5}$

Fig. 4. shows the measured breakthrough curves for the examined samples together with the fitted curves obtained using the POLLUTEv.6 program for different values of the parameters. The description of the curves in Fig. 4. is shown in Table 2.

In the calculation, one-dimensional advection-dispersion equation was applied for columns 1 and 4. The initial solution consisted only of the nonreactive tracer (Cl), therefore only the Darcy velocity and dispersion coefficient were changed, whereas the retardation mechanisms did not occur. The fitted curves for the Darcy velocity calculated from the flow value ( $v = 5.41 \cdot 10^{-6} \text{ m/s}$  for  $Q = 4.17 \cdot 10^{-8} \text{ m}^3/\text{s}$ ) did not correspond well with the measure points. This is the reason why this parameter was not established from both flow conditions and numerical modeling. The best fitted Darcy velocity for column 1 equals  $6.5 \cdot 10^{-6} \text{ m/s}$  and the dispersion coefficient is equal to  $2.5 \cdot 10^{-6} \text{ m}^2/\text{s}$ . For column 4 these parameters equal  $6.5 \cdot 10^{-6} \text{ m/s}$  and  $7 \cdot 10^{-7} \text{ m}^2/\text{s}$ , respectively.

In numerical calculations for columns 2, 3 and 5, the linear, Freundlich non-linear and Langmuir non-linear models were used. The initial Darcy velocity and dispersion coefficients were assumed as the initial values from the calculations of columns 1 and 4. Such estimated values of parameters were correct only for the linear sorption of copper in column 5. For other columns and solutions the Darcy velocity and dispersion coefficients were determined once again. It can be noticed that the breakthrough curves of  $\text{NH}_4^+$  for column 5 are not S-shaped. This may be explained by the occurrence of the retardation mechanisms other than sorption, in which ammonium is involved. In these examples, four-component solutions were used ( $\text{NH}_4^+$ ,  $\text{Cu}^{2+}$ ,  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$ ).

For the same sample, the breakthrough curve of copper was estimated. The four-component solution was also used in column 3; in this case, however, problems like the ones in column 5 have not been observed. Probably, this fact is the result of a different temperature, with the first experiment (column 5) carried out in the summer (20-26°C) and the second (column 3) - in the winter (19-22°C). High temperatures in the summer resulted in the degradation process. For the rest of the samples it was not difficult to determine the requested values. The linear model described the best relationships for columns 2 and 5 (copper), and the non-linear Langmuir model - for column 3. The retardation coefficient R was calculated for the linear sorption models using the relationship

$$R = 1 + \frac{\rho_d}{n_e} K_d, \quad (3.3)$$

where: R – retardation coefficient [-],  
 $\rho_d$  – dry density of the sample [ $\text{kg}/\text{m}^3$ ],  
 $n_e$  – effective porosity [-],  
 $K_d$  – partitioning coefficient from the linear sorption model [ $\text{m}^3/\text{kg}$ ].

The retardation coefficients R for columns 2, 3 and 5 (Cu) were equal to 63, 67 and 18 respectively.

## 5. CONCLUDING REMARKS

Numerical analyses of column experiments using the POLLUTEv.6 program allow to determine the breakthrough curves of contaminant transport through zeolite-sand mixtures well matching with the measured values. The disadvantage of POLLUTEv.6 is the limitation as to the modeling of the solution flow direction (from bottom to the top of the sample), just like in the

experiments. Parametric analysis of the column tests requires the knowledge of the influence of the parameters on the shape of the breakthrough curve. Moreover, POLLUTEv.6 does not provide statistical values, therefore it is difficult to estimate the accuracy of the model. Finally, it should be concluded that this program is helpful in interpreting the contaminant migration column tests.

### Acknowledgment

This research was partially supported by Grant No. 2P04G 088 29 from the Ministry of Science and Information Society Technology, Warsaw, Poland

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