

## Diffusion through Pulverized Stone Compared to Other Mineral Barrier Materials

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### Abstract

Construction of a waste disposal site requires an effective barrier that separates waste from a sub-base and minimizes the migration of contaminants from the site to an aquifer. Barrier layers most often used are natural clayey deposits or compacted clay liners and PEHD geomembranes. However, some regions, the Croatian karst for example, are mostly short of clay. For this reason, the use of pulverized stone, the by-product in the building-stone industry – as a potential liner material was investigated. Considering diffusion is an important mechanism of contaminant transport through barriers, this paper describes the method and apparatus for determining the diffusion coefficient of pulverized stone. Measured diffusion values were related to sample compaction and compared with the physical properties of clay, geosynthetic clay liners and PEHD geomembranes. Other physical properties of pulverized stone such as the filtration coefficient, density and particle size distribution are also presented. Finally, the suitability of pulverized stone for barrier construction is discussed based on the results obtained.

### 1. INTRODUCTION

Construction of a waste disposal site necessarily involves implementing an effective barrier which is intended to isolate waste from the sub-base and minimize the transport of contaminants from the site to an aquifer. Natural clayey deposits and compacted clay liners with PEHD geomembranes are the barrier liners that are generally used. But, in some regions, the Croatian karst for example, clay is not available in sufficient quantities and, consequently, other natural materials should be considered. Therefore, the use of pulverized stone (the by-product in the building-stone industry) as a potential liner material was investigated. The properties of pulverized stone were compared to those of the Novačica clay (the clay which was used for the barrier liner applied in the Jakuševac landfill) and of a geosynthetic clay liner (GCL), the material which is usually used in “clayless” regions.

The transport of contaminants through porous media such as clay, pulverised stone and a GCL, which are used as barriers, may be the result of only two physical processes, namely convection and molecular diffusion. Since migration of chemical substances through barriers caused by convection is negligible, diffusion is a dominant mechanism of contaminant transport. The transport (caused by diffusion) of an observed tracer in a solution can be described by Fick's first law (DAGAN, 1989):

$$q_m = -D_M \nabla c,$$

where:

$q_m$  is the flow of a tracer caused by diffusion [M/L<sup>2</sup>T],

$D_M$  is the diffusion coefficient of the observed matter in a given solvent [L<sup>2</sup>/T],

$\nabla$  is Hamilton's operator [1/L],

$c$  is the concentration of the observed tracer [M/L<sup>3</sup>].

The transport of contaminants in barrier liners caused by diffusion is slower than in a free solution because of the reduced cross-sectional area of flow and the more tortuous pathways for migration in a porous medium, i.e. barrier. In addition, the rate of transport can be further reduced by the interaction of the contaminants and the walls of the porous medium, i.e. absorption reactions. Hence, the effective diffusion coefficient ( $D_M^E$ ) should be defined as follows DAGAN (1989):

$$D_M^E = D_M f(n),$$

where:

$D_M^E$  is an effective molecular diffusion coefficient in a porous medium [L<sup>2</sup>/T],

$f(n)$  is a function dependent on a porous medium.

### 2. METHODS AND APPARATUS

The diffusion of contaminants in a saturated sample was studied under laboratory conditions ( $T=20^\circ\text{C}$ ) with NaCl solution as a tracer. Since the electrical conductivity of an NaCl solution of low concentrations is linearly proportional to the ion concentration in water, the NaCl concentration can be determined by measuring the electrical conductivity of the solution.

The apparatus for measuring diffusion (Fig. 1) consisted of two beakers of different sizes, placed one inside the other (ROWE et al., 1995). The inner

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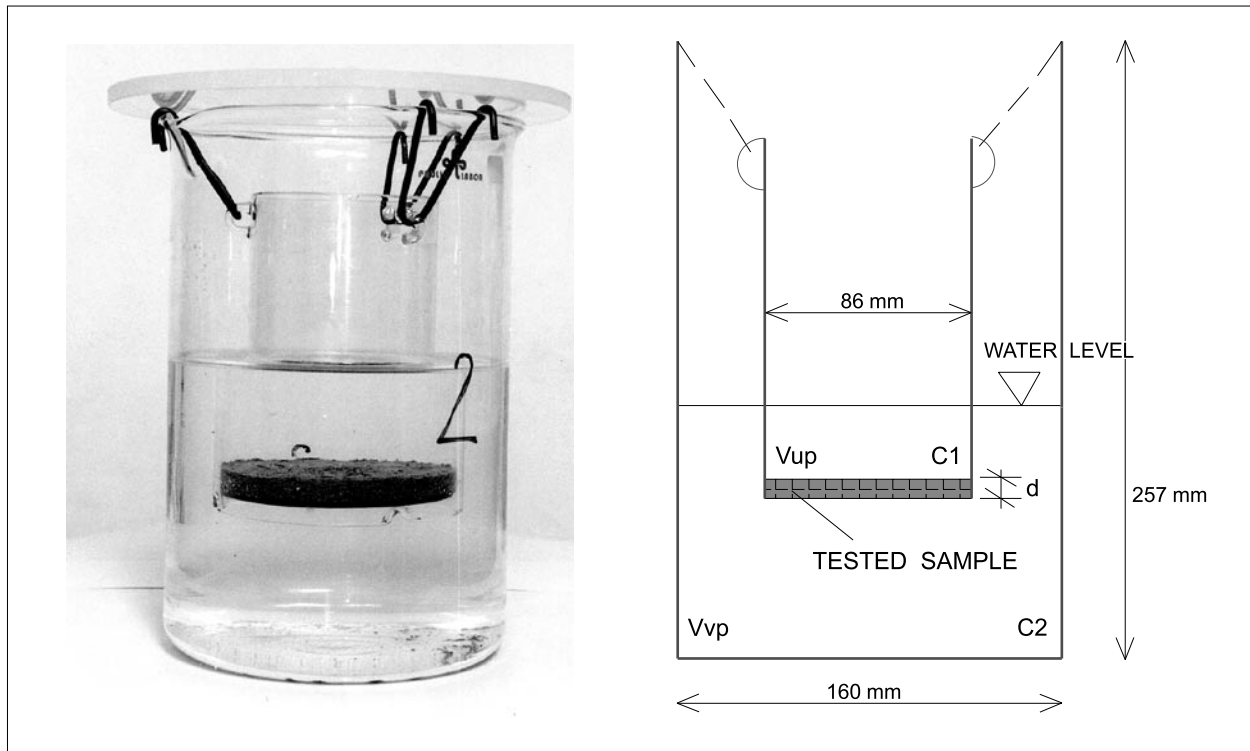


Fig. 1 The laboratory apparatus.

beaker with an inside diameter  $d=86$  mm and a height  $h=150$  mm was suspended from the rim of the outer beaker having an inside diameter  $d=160$  mm and a height  $h=257$  mm. The bottom of the inner beaker was removed, and a corrosion-resistant net or a piece of filter paper inserted instead to prevent the sample from scattering. Both beakers were made of laboratory glass that does not react with the solutions used for measurement. The beakers were filled with water, and the water surface in both beakers was maintained at the same level for the duration of measurement to prevent the transport of the tracer by convection.

The experiment started by feeding the given amount of the tracer into the inner beaker. Due to differences in the concentration of solutes on the sides of the sample (the concentration gradient), the tracer passed through the sample into the outer beaker. The rate of transport depends on the concentration gradient. The transport of the tracer through the sample can be described by Fick's law. The transport from the inner beaker through the sample ( $Q_1$ ) can be expressed as:

$$Q_1 = -DA \frac{\partial c}{\partial x},$$

where  $A$  is the effective sample area.

The transport from the outer side of the sample ( $Q_2$ ) is:

$$Q_2 = -DA \left( \frac{\partial c}{\partial x} + \frac{\partial^2 c}{\partial x^2} dx \right),$$

and thus the change in the tracer quantity in the sample is:

$$Q_1 - Q_2 = -DA \frac{\partial c}{\partial x} + DA \frac{\partial c}{\partial x} - DA \frac{\partial^2 c}{\partial x^2} dx = DA \frac{\partial^2 c}{\partial x^2} dx$$

on the basis of which a change in concentration in time can be expressed:

$$\frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2}.$$

The last equation is known as Fick's second law. This law was applied in this paper for solving the inverse problem, i.e. the diffusion coefficient was calculated on the basis of the measured change in concentration with time.

### 3. TESTED SAMPLES OF BARRIER LAYERS

#### 3.1. Pulverized stone

Barrier layers used for the construction of landfills are usually made of clay. However, clay is not available in sufficient quantities in some areas including the karst region for example. Therefore, the barrier properties of pulverized stone (refuse in the stone industry and a potential barrier material), were studied. It was expected that, in combination with some additives, pulverized stone could be used for the construction of barrier layers.

Consolidation pressure (kN/m <sup>2</sup> )	Filtration coefficient (cm/s)
50	$6.66 \times 10^{-7}$
100	$6.30 \times 10^{-7}$
200	$5.84 \times 10^{-7}$
400	$5.12 \times 10^{-7}$

Table 1 Filtration coefficients of the tested pulverized stone.

The physical properties of pulverised stone were found to be as follows: particle density  $\rho_s = 2.96 \text{ g/cm}^3$ , water content  $w = 33\%$ , liquid limit  $w_l = 46.24\%$ , plastic limit  $w_p = 29.04\%$ , and plasticity index  $I_p = 17.20\%$ . Figure 2 shows the particle-size distribution of the pulverized stone samples. The filtration coefficient was measured by VEINOVIĆ & KVASNIČKA (2000) and is given in Table 1 together with the consolidation pressure values.

Pulverized stone was inserted into the apparatus using a hammer and different compaction energies were applied, which resulted in dry densities of 1.55, 1.56 and  $1.57 \text{ g/cm}^3$  (Table 2). The sample thickness was measured after insertion and was  $1.2 \pm 0.1 \text{ cm}$ .

### 3.2. The Novačica Clay

For the purpose of determining the diffusion coefficient of the Novačica clay, the clay samples were compacted by applying the same three compaction energies as those applied to the pulverized stone; dry densities for pulverized stone and clay vs. degree of compaction are given in Table 2. It should be noted that the dry density of a well-compacted material is roughly equal to the maximum dry density obtained by compaction according to the Proctor standard.

The physical properties of the Novačica clay, obtained by testing, are as follows: particle density  $\rho_s = 2.72 \text{ g/cm}^3$ , natural water content  $w = 21.0\%$ , liquid limit  $63.5\%$ , plastic limit  $21.2\%$  and plasticity index

Degree of compaction	Pulverized stone density	Clay density
poorly compacted	1.55	1.77
well compacted	1.56	1.92
very well compacted	1.57	1.96

Table 2 Degree of compaction versus sample density ( $\text{g/cm}^3$ ).

42.3%. Filtration coefficient is  $1.32 \times 10^{-10} \text{ m/s}$ . Hence, the Novačica clay meets all the requirements set by designer for barrier layers.

### 3.3. Geosynthetic clay liner (GCL)

In addition to the diffusion coefficients of clay and pulverized stone, the research dealt with determining the effective diffusion coefficient of a commercially available GCL.

After being saturated with water under laboratory conditions, the tested GCL sample may experience significant changes in volume and, as a result of this, a change in properties. For this reason, the measuring apparatus was further equipped with two steel plates to prevent the sample from undesirable swelling. As compared to other tests in this paper, there was no possibility of testing samples with different densities, only the effective diffusion coefficient value is presented.

### 3.4. Sand–clay gel-mixture (TRISOPLAST®)

Among the alternative materials for barriers, a coefficient of diffusion for a single sand–clay gel mixture was measured. The chosen product was an industrial material called TRISOPLAST®, produced with a patented technology developed by GID Milieutechniek (The Netherlands; [www.trisoplast.nl](http://www.trisoplast.nl)). The material consists of a clay gel mixed with a filler, e.g. sand. As soon as water penetrates the mixture, the clay gel is formed

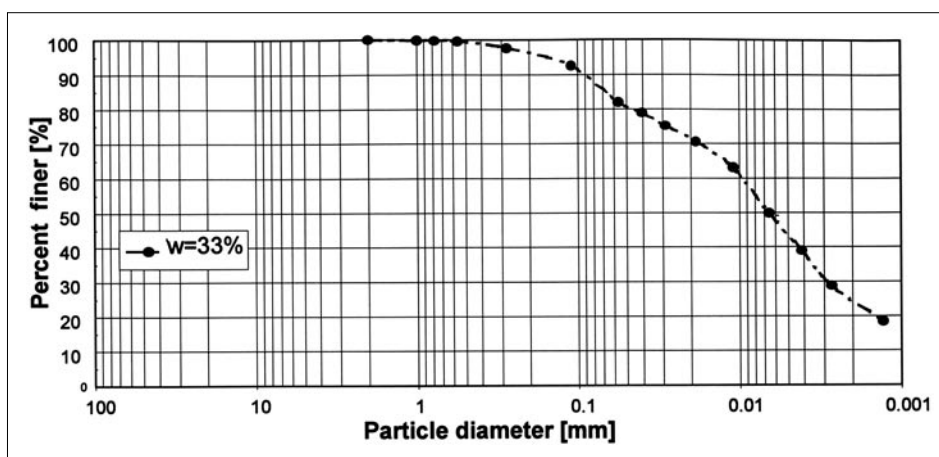


Fig. 2 A particle-size distribution curve of pulverised stone.

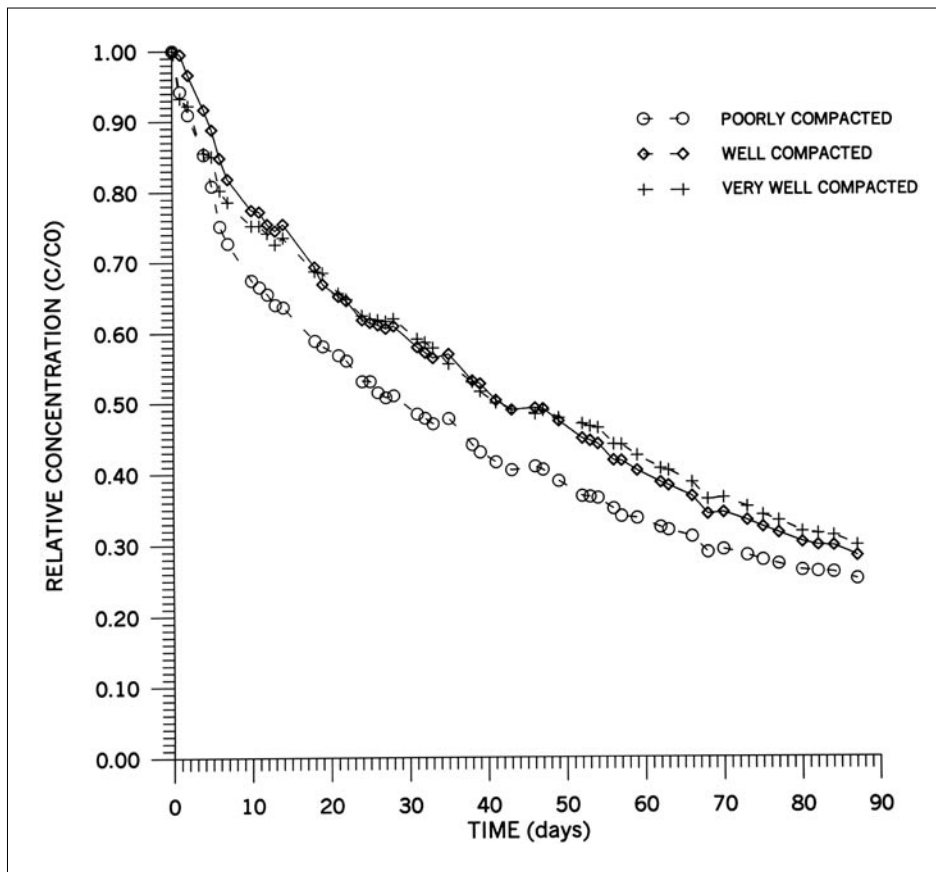


Fig. 3 Changes in solute concentration in the inner beaker for the pulverized stone sample.

from a mixture of clay minerals (bentonite) and polymers. A dense gel structure is created as a result of the presence of a network of chemical bonds between the clay mineral particles and polymers. The mixture has better barrier properties than traditional mineral barriers and it also allows far less water to permeate through it (at least 100 to 1,000 times less than traditional mineral barriers).

The mixture is used as a barrier in landfills, industrial sites, tank farms, reservoir basins, washing facilities, manure storage, etc. The producer suggests much thinner sealing layers can be used than those required for standard clay liners, because the mixture has a very low permeability. It is very plastic, with chewing-gum-like properties. When traditional mineral sealing materials are used, insufficient plasticity means that cracks can occur in the sealing layer if there is rapid and irregular subsidence. As the layer of the mixture can deform and stretch, it is able to follow soil deformation and subsidence. The large swelling capacity of the clay gel gives the mixture a large self-healing capacity in the event of damage. At the same time, clay minerals cannot be washed out because of the bonds with polymers.

According to WEITZ et al. (1997) the plastic limit of the mixture is 36%, the liquid limit is 179% and therefore, the plasticity index is 143%. The Proctor dry density for the standard mixture is 1.680 g/cm<sup>3</sup>, and the optimum water content is 16%. In the same report, the average diffusion coefficient was reported to be

4.0x10<sup>-10</sup> m<sup>2</sup>/s. The diffusion coefficient for chloride varies from 1 to 8x10<sup>-10</sup> m<sup>2</sup>/s.

### 3.5. PEHD geomembrane

This research did not include testing of a PEHD geomembrane; the only reason was because the apparatus used was unsuitable for measuring the diffusion coefficient of the PEHD geomembrane, as its value is much lower than those of the other tested materials for which the apparatus was originally designed. For information, the diffusion coefficients for the transport of toluene and xylene through the PEHD geomembrane found in professional literature are  $D_M^E = 5.1 \times 10^{-13}$  m<sup>2</sup>/s and  $D_M^E = 1.0 \times 10^{-13}$  m<sup>2</sup>/s respectively (PRASAD et al., 1994).

## 4. MEASUREMENT RESULTS

As the measuring technique was found to be suitable for this research, the diffusion coefficient tests were carried out for the samples of clay from the Novačica site, pulverized stone, TRISOPLAST® and the GCL. Exact density values of the sample materials, the water volume in both the inner and outer beakers, and the temperature and change in electrical conductivity were measured in each test.

The measuring apparatus was set after the sample

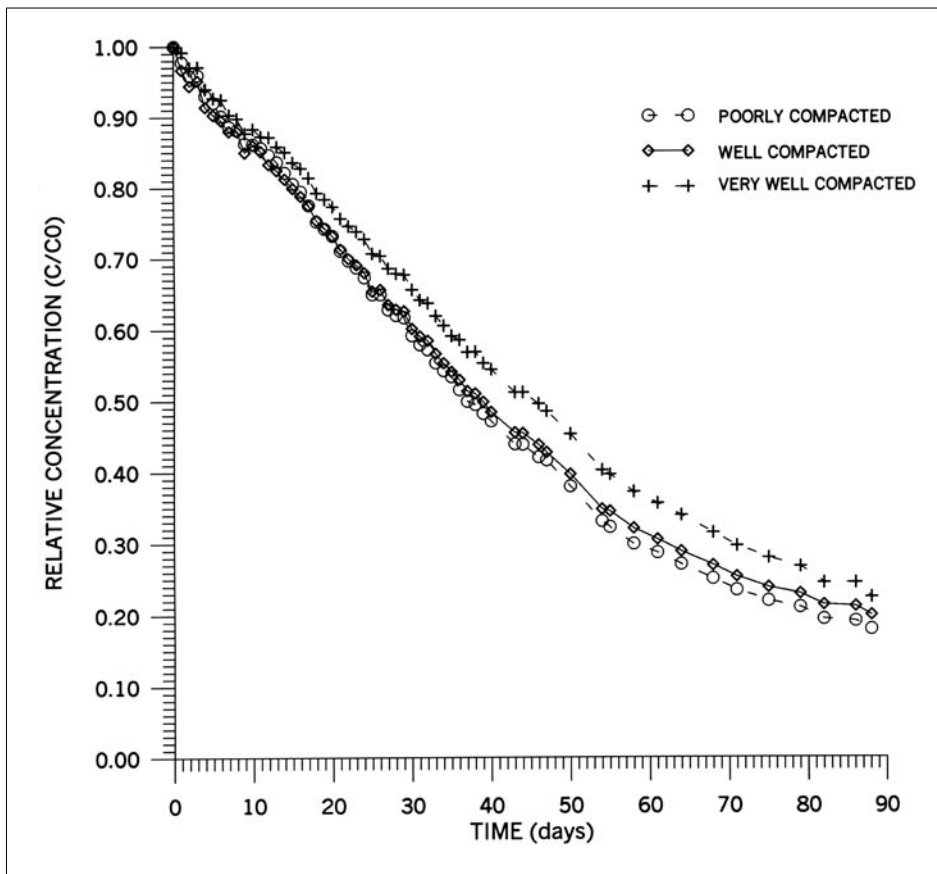


Fig. 4 Change in NaCl concentration in the inner beaker for the clay sample.

was inserted and water added to achieve steady state conditions. Then, 2 g of NaCl were fed into the inner beaker, which resulted in the increase in concentration of the solution contained in the inner beaker. The rate of reduction in concentration of solutes in the inner beaker with time was measured (Fig. 3). The gradual increase in ion concentration in the outer beaker over the next few days was measured.

Based on the research results, the mean values of the effective diffusion coefficient for pulverized stone were measured (Table 3).

The same test was carried out with clay used for barrier liners. The results are shown in Fig. 4 which presents a decrease in the tracer concentration in the inner beaker for three samples which were inserted by applying different compaction energies. The graph shows that the clay sample having highest density is the least permeable, as expected.

A mean value of the effective diffusion coefficient for the Novačica clay was calculated on the basis of the test results (Table 3).

The effective diffusion coefficient was also measured for TRISOPLAST®. The results are shown in Fig. 5 and Table 3. The graph shows that all three samples, compacted to different densities, have almost the same effective diffusion coefficient.

In addition to pulverized stone, and TRISOPLAST®, a sample of GCL was also tested using the same measuring apparatus. Based on the measurements taken and the interpretation of the results, the effective diffusion coefficient of GCL was computed as  $D_M^E = 6.06 \times 10^{-10} \text{ m}^2/\text{s}$ .

These results are shown in Table 3 together with the effective diffusion coefficient values for the PEHD geomembrane taken from the literature. Compaction vs.

Degree of compaction	Pulverized stone	Clay	TRISOPLAST®	GCL	PEHD geom.
poorly	$3.22 \times 10^{-10}$	$2.06 \times 10^{-10}$	$2.64 \times 10^{-10}$	$6.06 \times 10^{-10}$	$5.1 \times 10^{-13}$ to $1.0 \times 10^{-13}$
well	$2.92 \times 10^{-10}$	$1.98 \times 10^{-10}$	$2.59 \times 10^{-10}$		
very well	$2.38 \times 10^{-10}$	$1.78 \times 10^{-10}$	$2.60 \times 10^{-10}$		

Table 3 Effective diffusion coefficients,  $D_M^E$  (in  $\text{m}^2/\text{s}$ ) of different barrier materials.

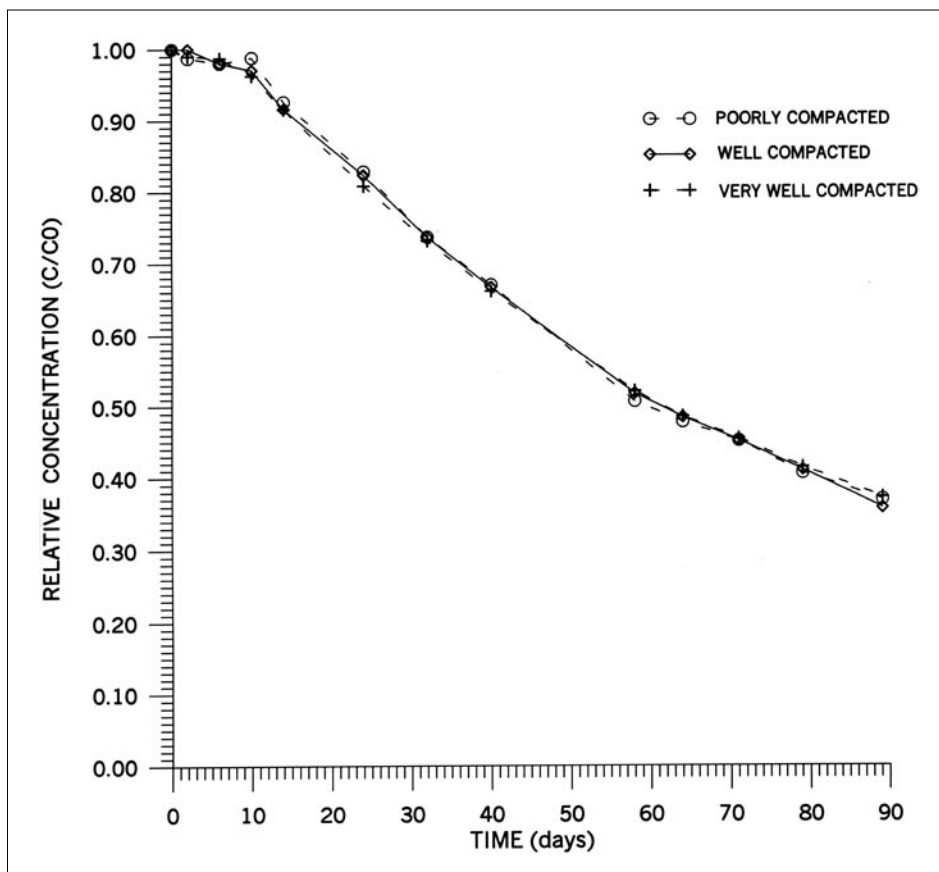


Fig. 5 Change in NaCl concentration in the inner beaker for TRISOPLAST®.

effective diffusion coefficients,  $D_M^E$ , for different barrier materials are presented in Fig. 6.

While samples of clay, pulverized stone and TRISOPLAST® have similar values, the GCL diffusion coefficient was two orders of magnitude lower than that of the other tested materials.

## 5. CONCLUSIONS

When making a decision on the selection of a material for a barrier liner to be used in sanitary landfills, it is also necessary to be aware of the quantity of contaminants transported due to the diffusion process. Although the quantity of contaminants transported in this way is relatively low, this quantity can be important in the case of highly toxic substances or for nearby aquifers holding low water quantities.

The transport of substances induced by diffusion is defined by Fick's laws that explain that the transported quantity of contaminants depends on the effective diffusion coefficient of a barrier layer, i.e. the shape and volume of pores, and also the thickness of the layer. The paper deals with test results carried out to determine effective diffusion coefficients for clay from the Novačica site, pulverized stone (the by-product in the stone industry), TRISOPLAST® and a type of GCL in commercial use. For the purposes of measurement, an

apparatus intended for these materials was designed. The results obtained were compared with data on the effective diffusion coefficient of a PEHD geomembrane taken from literature.

In sample preparation, different compaction energies were applied and the relationship between the diffusion coefficient and the compaction of the sample was observed. As the sample compaction increased so the effective molecular diffusion coefficient decreased, which was particularly noticeable in the case of pulverized stone.

Well-compacted pulverized stone has an effective molecular diffusion coefficient roughly equal to that of clay and, therefore, can be used for the construction of barrier liners. Prior to applying pulverized stone for barrier liners, the transport of pollutants by convection should be studied. If necessary, additives or some other technical solutions should be applied to prevent possible pollutant transport through the pulverized stone liner.

Considering its use in barriers, as opposed to industrial products, pulverised stone is expected to be built in a thick layer, as much as 1.0 m or more (like clay). Although the diffusion coefficients of pulverised stone and industrial products are of similar values, because of the layer thickness, cumulative diffusion transport through the pulverised stone layer should be much less than the transport through industrial products.

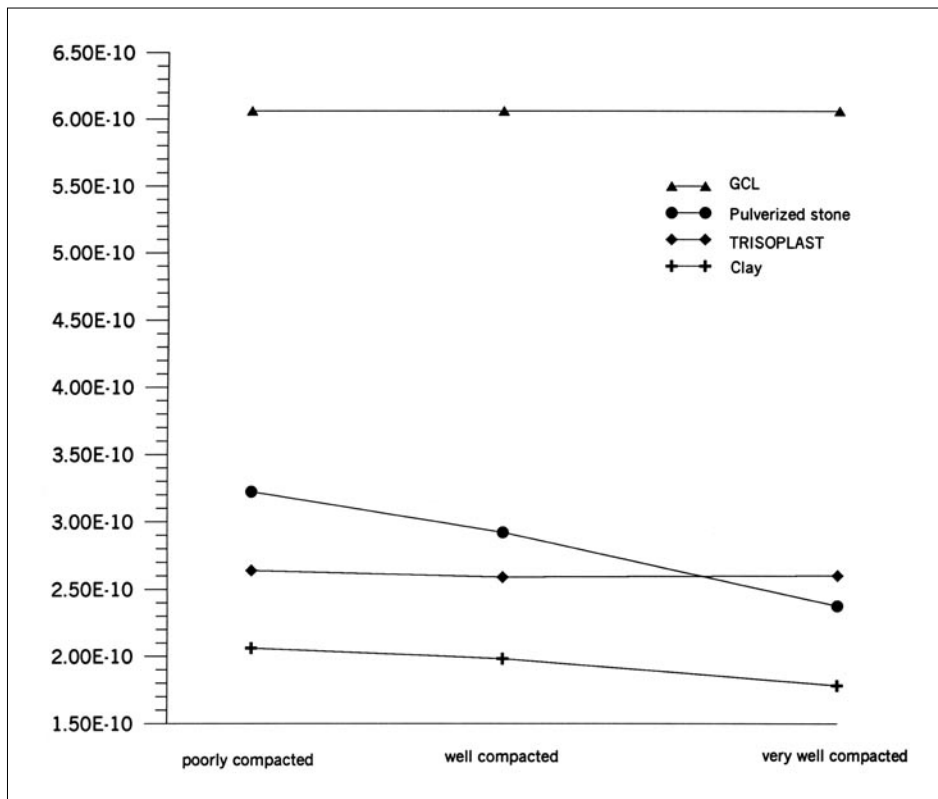


Fig. 6 Compaction vs. effective diffusion coefficient values,  $D_M^E$ , for different barrier materials.

## 6. REFERENCES

- DAGAN, G. (1989): Flow and transport in porous formations.– Springer-Verlag, Berlin, 465 p.
- PRASAD, T.V., BROWN, K.W. & THOMAS, J.C. (1994): Diffusion coefficients of organics in high density polyethylene.– Waste Management & Research, 12, 61–71.
- ROWE, R.K., QUIGLEY, R.M. & BOOKER, R.J (1995): Clayey barrier systems for waste disposal facilities.– E&FN Spon, London, 390 p.
- VEINOVIĆ, Ž. & KVASNIČKA, P. (2000): Possible application of waste stone dust for sanitary landfill liners.– VI<sup>th</sup> International Symposium Waste Management – Zagreb 2000, Proceedings, 1, 323–332.
- WEITZ, A.M., BOELS, D. WIEGERS, H.J.J. & EVERS-VERMEER, J.J. (1997): Application of TRISOPLAST for lining of landfills.– Winand Staring Centre for Integrated Land, Soil and Water Research, Agricultural Research Department, Report 142, Wageningen.

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