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Effective Diffusion Coefficient: From Homogenization to Experiment

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Abstract. In this paper, an example of the application of the homogenization approach (asymptotic expansion technique) to predict the effective diffusion coefficient for an equivalent continuum, together with the experimental verification of the theoretical results is presented. The experimental setup was constructed for the measurements of diffusion in a model periodic porous medium made of Plexiglas. The computer program using the FEM was elaborated to solve the local boundary value problem for a period and to calculate the effective diffusion coefficient. The comparison between the theory and the experiment indicates good agreement between the numerical and experimental values of the effective diffusion coefficient. Interpretation of the test data from the point of view of the homogenization theory is also incorporated.

Key words: effective diffusion coefficient; model test, numerical calculations, homogenization

Notations

c	solute concentration.
c_c, t_c, D_c	characteristic quantities.
D	molecular diffusion coefficient.
D^{eff}	effective diffusion coefficient.
l	characteristic microscopic length.
L	sample length.
n	porosity.
$\mathcal{L}$	characteristic macroscopic length.
x_i	macroscopic nondimensional variable.
y_i	microscopic nondimensional variable.
X_i	physical variable.
N	unit outward vector normal to Γ.
S	volume of the pores in the period divided by the length of the period.
t	time variable.
t^*	nondimensional time variable.
V	volume of the liquid in the reservoir.
ε	homogenization (or scale separation) parameter.
ε_g	geometrical scale separation parameter.

χ_i	local vector field.
χ_i^*	nondimensional local vector field.
Ω_l	volume of the pores in the period.
Ω_s	volume of the solid in the period.
Ω	total volume of the period $(\Omega = \Omega_l + \Omega_s)$.
Γ	boundary between Ω_l and Ω_s.

1. Introduction

The knowledge of effective diffusion coefficient is of paramount importance for the calculations of diffusive transport in porous media. This kind of transport is met in many different domains. For example, recent studies have indicated that diffusion is the controlling mechanism of contaminants transport through soil barriers (soil liners and slurry walls). Failure to recognize the role of diffusion in barrier design used for waste containment can lead to extremely unconservative designs (Manassero and Shackelford, 1994). In general, diffusion is a well-recognized phenomenon and diffusion coefficients for solute diffusion in free solution (also called molecular diffusion coefficients) are available in the literature for most chemical compounds. The problem arises when diffusion occurs in a porous medium, where the presence of solid matrix restricts the (random in nature) movements of molecules to the pore space. In such cases, the evaluation of the effective diffusion coefficient becomes more complicated.

The theoretical approaches to the problem of the determination of the effective diffusion coefficient are based on ‘the micro–macro passage’ (the homogenization). The general idea of the homogenization process consists of the passage from the description of the phenomena at the microscale (the local scale), where the medium is heterogeneous and the governing equations are known, to the equivalent macroscopic continuum that provides the ‘averaged’ behaviour of the medium. The main advantage of this approach is the ‘elimination’ of the microscopic scale, in favor of the macroscopic one, over which the variables such as the concentration or the velocity are measured. In this framework the effective diffusion coefficient for the macroscopic transport equation can be directly calculated, provided the microscopic structure of the porous medium, i.e., the geometry of the pores is known. Unfortunately, at present such calculations are practically impossible for most of the actual porous media (like soils), due to very complex, and often not well defined, pores networks. The existing techniques are not powerful enough to deal with actual porous media and the only way to estimate the effective diffusion coefficient is through experimentation.

Several approaches are used for the measurement of the effective diffusion coefficient. A comprehensive review of the methods suitable for soils can be found in Shackelford and Daniel (1991); Manassero and Shackelford (1994). During the experimental process, known initial and boundary conditions are imposed to a representative sample of the medium. That provokes the transport phenomena to occur, that means the propagation of the solute into the soil. The response of the system, i.e., the concentration as a function of space and time variables is monitored. Then, the effective diffusion coefficient is fitted to the transport equation so, that the difference between the concentration predicted and the one observed in the experiment is sufficiently small. At that point the important condition of the applicability of the transport equation should be recalled. It can be formulated as follows: the transport equation treating the porous medium as a continuum is valid, provided the homogenizability conditions for the medium and the phenomena are met (see relation (4) below). If these conditions are not satisfied, the experiment will not lead to the determination of the intrinsic diffusion parameter (Auriault and Lewandowska, 1996).

In this paper, the problem of theoretical and experimental evaluation of the effective diffusion coefficient for a periodic porous medium will be addressed. The purpose of the paper is to present an example of the application of the homogenization approach to predict the effective parameters of the equivalent continuum, together with the experimental verification of the obtained theoretical results. Owing to the homogenization approach the complete resolution of the problem could be captured.

2. Formulation of the Problem

Let us consider diffusion phenomenon occurring in a periodic porous medium shown in Figure 1. It is assumed that the solid part in the period is undeformable and impermeable. The pores are fully saturated by an incompressible fluid containing a solute of the concentration c. There is neither adsorption of the solute on the solid surface nor any reaction. Our objective is the theoretical and the empirical evaluation of the effective diffusion coefficient for such a medium.

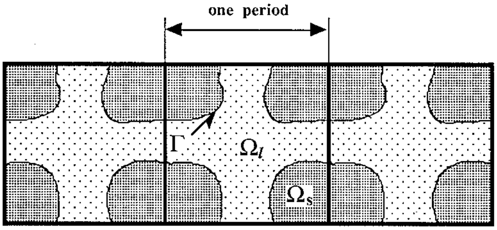

Figure 1. Periodic porous medium.

3. Homogenization Approach

The starting-point of the homogenization analysis is the description of the physical process taking place in the pores of the porous medium. It is assumed that Fick's molecular diffusion in the pores can be described by the following mass balance equation for the nondimensional variables (Auriault and Lewandowska, 1993)

$$P\frac{\partial c^*}{\partial t^*} + \frac{\partial}{\partial y_i}\left(-D^*_{ij}\frac{\partial c^*}{\partial y_j}\right) = 0, \tag{1}$$

with the boundary condition imposed on the solid–liquid interface

$$-N_i\left(D^*_{ij}\frac{\partial c^*}{\partial y_j}\right) = 0 \quad \text{on } \Gamma, \tag{2}$$

where the superscript '*' denotes the nondimensional variables. **N** is the unit outward vector normal to Γ. In the derivation of Equations (1) and (2) the following representation of the variables is introduced

$$\begin{aligned}
&\text{concentration}: \quad c = c_c c^*,\\
&\text{space variable}: \quad \mathbf{X} = l\mathbf{y}\\
&\text{time variable}: \quad t = t_c t^*,\\
&\text{molecular diffusion tensor}: \quad D = D_c D^*,\\
&\text{dimensionless number}: \quad P = \frac{l^2}{t_c D_c}.
\end{aligned} \tag{3}$$

The subscript 'c' means the characteristic quantity (constant). The parameter ε appearing in Equation (1) is the ratio of the characteristic microscopic length l (dimension of a period) to the macroscopic length L (dimension of a porous sample). The very important assumption is the scale separation assumption expressed as follows

$$\varepsilon = \frac{l}{L} \ll 1. \tag{4}$$

For a transient equivalent macroscopic description to be possible, the dimensionless number must verify (Auriault and Lewandowska, 1993)

$$P = \mathrm{O}(\varepsilon^2). \tag{5}$$

The characteristic lengths l and L introduce two nondimensional space variables

$$\mathbf{x} = \frac{\mathbf{X}}{L}, \qquad \mathbf{y} = \frac{\mathbf{X}}{l}. \tag{6}$$

Due to the separation of scales the concentration is the function of three variables $c = c(\mathbf{x}, \mathbf{y}, t)$, where $\mathbf{x} = \mathbf{x}(x_1, x_2, x_3)$ and $\mathbf{y} = \mathbf{y}(y_1, y_2, y_3)$. The problem will be investigated by means of the asymptotic expansion method which is often used to derive the macroscopic equivalent models for finely heterogeneous materials, like porous media, composite materials, etc. (Bensoussan *et al.*, 1978; Sanchez-Palencia, 1980; Auriault, 1991). When following the homogenization technique, it is assumed that the concentration can be presented in the form of an asymptotic expansion

$$c^*(\mathbf{x},\mathbf{y},t^*) = c^0(\mathbf{x},\mathbf{y},t^*) + \varepsilon^1 c^1(\mathbf{x},\mathbf{y},t^*) + \varepsilon^2 c^2(\mathbf{x},\mathbf{y},t^*) + \cdots \tag{7}$$

where the components $c^i(\mathbf{x},\mathbf{y},t^*)$ are **y**-periodic and the variable **x** is expressed by the variable **y**, i.e. $\mathbf{x} = \varepsilon\mathbf{y}$. Note that the gradient operator becomes

$$\frac{\partial(.)}{\partial y_i} \to \frac{\partial(.)}{\partial y_i} + \varepsilon\frac{\partial(.)}{\partial x_i}. \tag{8}$$

The methodology of the homogenization resides in the application of the asymptotic expansion (7) to Equations (1) and (2). Comparison of the terms of the same powers of ε will yield the required descriptions in the form of the systems of equations to be analysed. In result, after transformations that are presented in details in the paper by Auriault and Lewandowska (1993), the following macroscopic governing equation is obtained

$$n\frac{\partial c^*}{\partial t^*} + \frac{\partial}{\partial x_i}\left(-D_{ij}^{\mathrm{eff}^*}\frac{\partial c^*}{\partial x_j}\right) = \mathrm{O}(\varepsilon), \tag{9}$$

where $\mathbf{D}^{\mathrm{eff}^*}$ is the effective (or macroscopic) diffusion tensor and n is the porosity

$$n = \frac{|\Omega_l|}{|\Omega|}.$$

$\mathbf{D}^{\mathrm{eff}^*}$ is defined by the volume average

$$D_{ij}^{\mathrm{eff}^*} = \frac{1}{|\Omega|}\int_{\Omega_l} D_{ik}^*\left(I_{kj} + \frac{\partial\chi_j^*}{\partial y_k}\right)\mathrm{d}\Omega. \tag{10}$$

The vector field χ^* is the solution of the following local boundary-value problem for the period

$$-\frac{\partial}{\partial y_i}\left[D_{ij}^*\left(I_{jk} + \frac{\partial\chi_k^*}{\partial y_j}\right)\right] = 0, \tag{11}$$

$$-N_i\left[D_{ij}^*\left(I_{jk} + \frac{\partial\chi_k^*}{\partial y_j}\right)\right] = 0 \quad \text{on } \Gamma, \tag{12}$$

where **I** is the identity tensor and $\chi_i^* = \chi_i^*(\mathbf{y})$ is **y**-periodic and its average over the period is zero

$$\langle\chi_i^*\rangle = \frac{1}{|\Omega|}\int_{\Omega_l}\chi_i^*\,\mathrm{d}\Omega = 0. \tag{13}$$

Remark that the Problem (11)–(13) depends uniquely on the microscopic features of the period geometry. It is independent of the boundary conditions imposed on the macroscopic external boundaries of the porous medium. Therefore, $\mathbf{D}^{\mathrm{eff}^*}$ is considered as an intrinsic parameter. It can be easily shown that $\mathbf{D}^{\mathrm{eff}^*}$ is symmetric and positive definite.

4. Numerical Calculations

The calculations of the effective diffusion tensor will be performed for the porous medium, periodic in one macroscopic dimension, Figure 2. We consider the period geometry as shown in Figure 3. This medium was primary used by Borne (1983) for the investigations of dynamic filtration. Let us assume the molecular diffusion tensor D as isotropic, $D_{ij} = DI_{ij}$. The axes X_1, X_2 and X_3 are the principal directions of the tensor D^{eff}, therefore it can be written

$$D^{\mathrm{eff}} = \left| \begin{array}{ccc} D_{11} & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & D_{33} \end{array} \right|_{X_1, X_2, X_3} . \tag{14}$$

To calculate the components of the effective diffusion tensor, the local boundary-value Problem (11)–(13) has to be solved. This problem consists of three independent equations for three components of the vector field χ^*. The equation ‘k’, i.e. the equation for the component χ_k^*, corresponds to the macroscopic gradient of the concentration in the direction ‘k’. Obviously, in the case considered we have, as in Auriault and Lewandowska (1993), $D_{22} = 0$ and $D_{33} = nD$. We turn to the determination of D_{11}. The local boundary-value problem for $\chi = \chi_1^*$ in the period is as follows

$$\frac{\partial^2 \chi}{\partial y_1^2} + \frac{\partial^2 \chi}{\partial y_2^2} = 0, \tag{15}$$

$$N_1 \left(1 + \frac{\partial \chi}{\partial y_1} \right) + N_2 \frac{\partial \chi}{\partial y_2} = 0 \quad \text{on } \Gamma, \tag{16}$$

$$\int_{\Omega_l} \chi \, \mathrm{d}\Omega = 0, \tag{17}$$

χ is Ω-periodic. Due to the arbitrary periodicity in the y_3 direction, it is a function of y_1 and y_2 only.

Remark that the problem is two-dimensional and the period is completely defined by its cross-section by the plane (X_1, X_2), Figure 4. The analysis of the geometrical symmetry of the period with respect of $y_1 = 0.5$ enables the simplification of the Problem (15)–(17). It is possible to show that the symmetry imposes

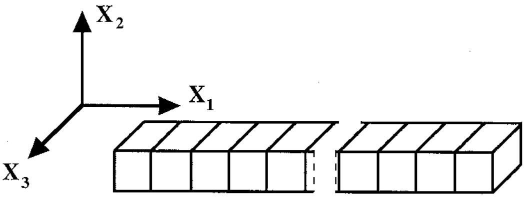

Figure 2. Periodic medium.

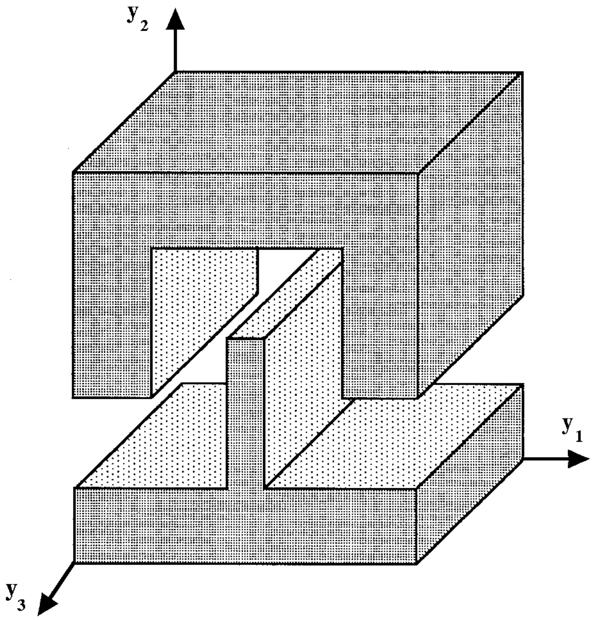

Figure 3. Geometry of the period.

χ to be an odd function of the variable $(y_1 - 0.5)$. Together with the periodicity of χ, it yields

$$\chi(y_1 = 0) = 0, \tag{18}$$

$$\chi(y_1 = 0.5) = 0. \tag{19}$$

The boundary-value problem is now formulated for the dimensionless half-period $0 \leqslant y_1 \leqslant 0.5$, Figure 5, as follows: find $\chi(y_1, y_2)$ satisfying Equations (15), (16), (18) and (19). This is a classical Laplace problem with particular boundary conditions. The problem was solved using the Finite Element Method (Schmelter, 1980). The domain Ω_l was divided into triangular elements. We applied the finite element mesh used by Borne (1983), Figure 6. This mesh is obtained by the conform transformation method. The network consists of 100 nodes and 144 elements.

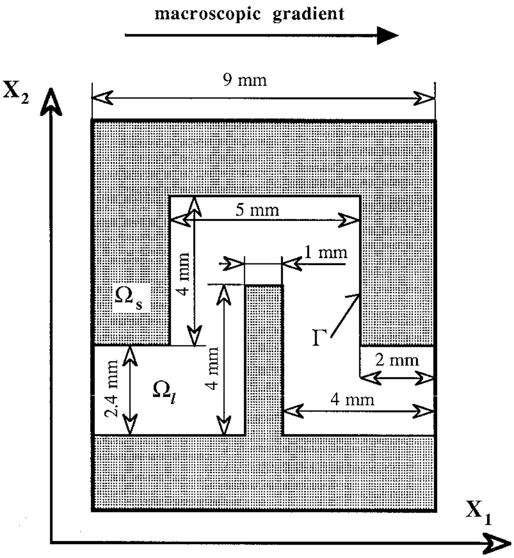

Figure 4. Cross-section of the period.

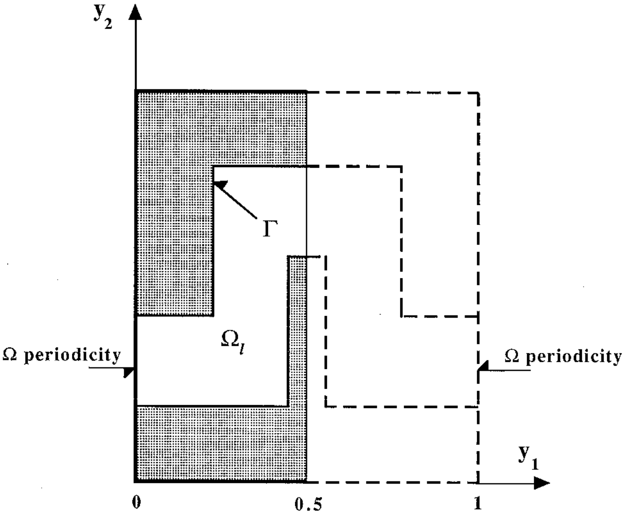

Figure 5. Dimensionless half-period.

Once the χ-field is known, the effective diffusion coefficient D_{11} can be calculated according to its definition given by Equation (10).

A computer program in Pascal was developed to solve the above problem. For the geometry of the period shown in Figure 5 we obtain the χ-field shown in Figure 7 and the effective diffusion tensor in the form

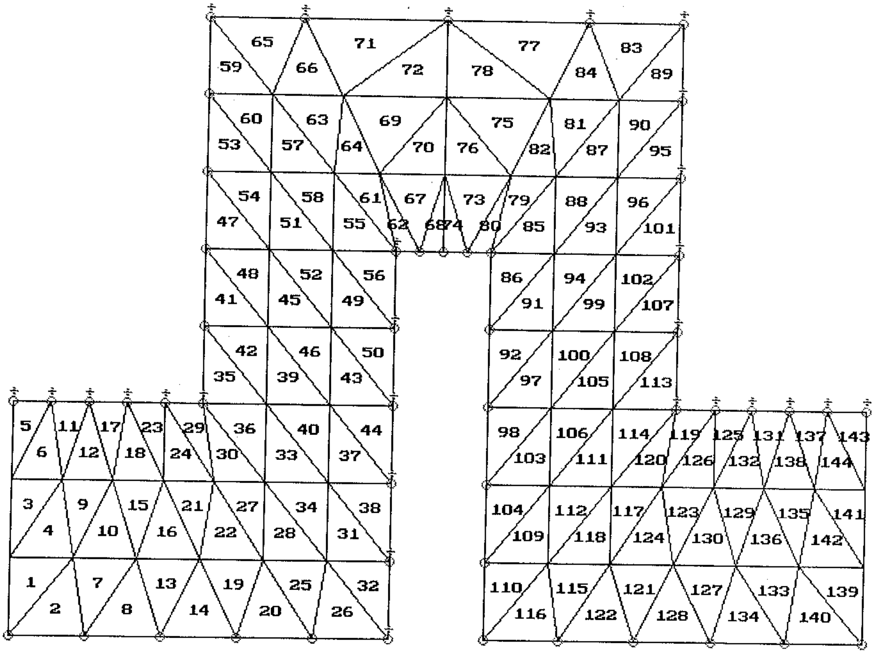

Figure 6. Final element mesh.

$$D^{\mathrm{eff}} = nD \begin{vmatrix} 0.3833 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 1 \end{vmatrix} . \tag{20}$$

To determine completely the numerical value of the effective diffusion coefficient, one has to know the molecular diffusion coefficient for NaCl solution at the concentration 0.017 mol/l and at the temperature 18.66°C. The following data are available

- at the concentration 0.017 mol/l and at 18°C, $D = 1.345 \times 10^{-5}$ cm^2/s (Landolt and Bornstein, 1935)
- at the concentration 0.017 mol/l and at 25°C, $D = 1.538 \times 10^{-5}$ cm^2/s (Zbior wielkosci fizyko-chemicznych, 1974).

The temperature dependence of D is assumed to be in the form (Kalendarz chemiczny, 1954)

$$D = D_0 \exp\left(-\frac{E}{RT}\right), \tag{21}$$

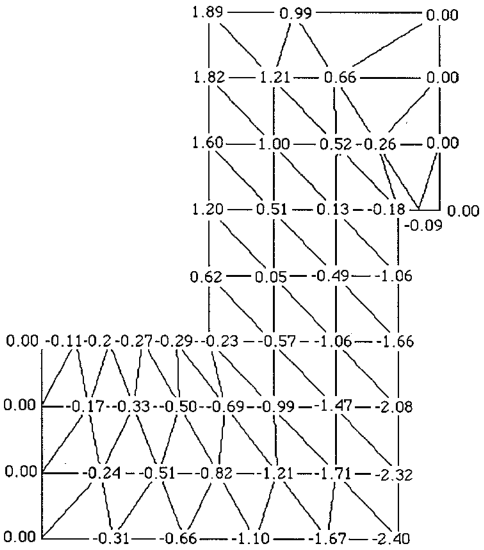

Figure 7. χ-field.

where E is the activation energy, T is the absolute temperature and R is the universal gas constant, $R = 8.134510(\mathrm{J}/^\circ\mathrm{K\,mol})$. The temperature interpolation for 18.66°C, according to Equation (24), gives

$$D = 1.362 \times 10^{-5}\,\mathrm{cm}^2/\mathrm{s}. \tag{22}$$

By using the above value of the molecular diffusion coefficient Equation (20) gives the effective diffusion coefficient in the X_1 direction

$$D_n^{\mathrm{eff,\,num}} = \frac{D_{11}}{n} = 5.22 \times 10^{-6}\,\mathrm{cm}^2/\mathrm{s}. \tag{23}$$

5. Experimental Investigations

The aim of this research was the experimental determination of the effective diffusion coefficient of the periodic porous medium described in Section 4. The solute concentration verifies

$$D_n^{\mathrm{eff}} \frac{\partial^2 c}{\partial X^2} = \frac{\partial c}{\partial t}, \tag{24}$$

where

$$D_n^{\mathrm{eff}} = \frac{D^{\mathrm{eff}}}{n} = \frac{D_{11}}{n}. \tag{25}$$

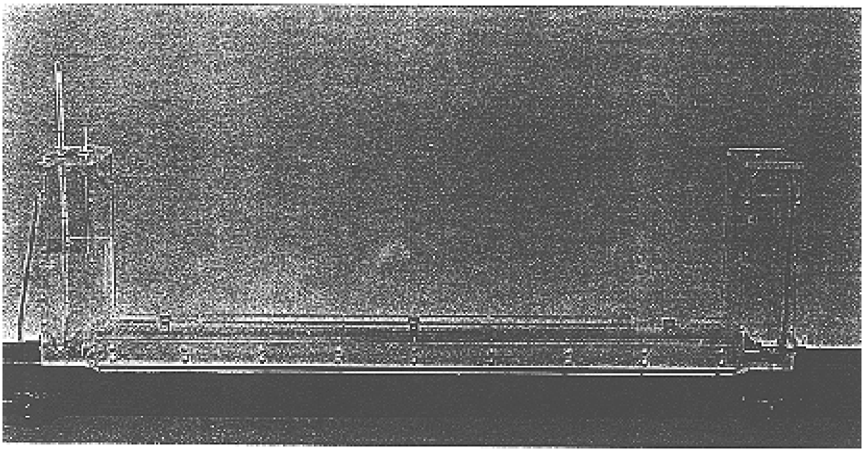

Figure 8. Experimental setup.

There exist several methods of measuring effective diffusion coefficient of miscible solute (Shackelford and Daniel, 1991; Manassero and Shackelford, 1994). The single reservoir with decreasing source concentration (SRDC) method was chosen for its relative simplicity.

5.1. THE SETUP

The experimental setup is presented in Figure 8 while its schematic view is shown in Figure 9. It consists of a Plexiglas model, periodic in the direction X_1 and placed between two reservoirs made of Plexiglas as well. The dimension in the direction X_3 is sufficiently large to justify the assumption that the microscopic problem is two-dimensional. In Borne, 1983 the ‘border effects’ for this geometry were evaluated to be of negligible importance. In the longitudinal direction X_1 there are 100 periods. Therefore, the geometrical scale separation parameter ϵ, according to Equation (4), is equal to 10^{-2}.

5.2. EXPERIMENT CONDITIONS

The model is equipped with two special valves on both sides of the model. First, the two valves were open and pure water (of resistivity 18.2 megaohms) was poured to saturate the model (pore volume $= 451.17\,\text{cm}^3$). It was left for 24 hours for the temperature to stabilize. Then, the two valves were closed and the reservoirs were emptied. Next, $1000\,\text{cm}^3$ of a NaCl solution (1 g of (dried) NaCl per kg of solution) was introduced into the left reservoir. A low concentration solution was used to avoid the influence of density variations (see: Jacob Bear and Arnold Verruijt *Modeling Groundwater Flow and Pollution,* D. Reidel, 1987). After 24 hours, the left valve was opened and the experiment started. Initial solution samples were taken for chemical analyses of the ion concentrations. An automatic burette of

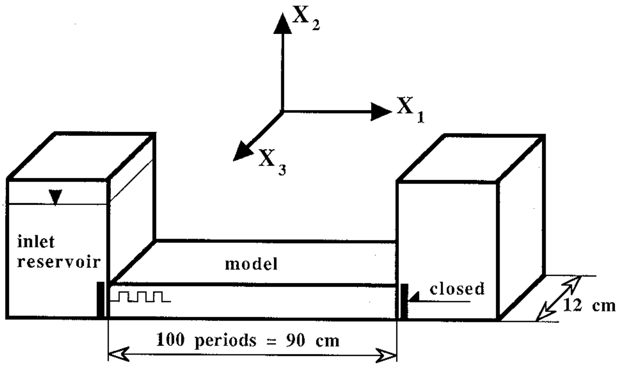

Figure 9. Schematic view of the experimental setup.

200 μl was used for sample withdrawals. The following chemical methods were used to analyze the samples

- cations Na^+:
  flame photometry FLAPHO 4 Carl Zeiss Jena.
- anions Cl^-:
  potentiometric titration with ion selective electrode $E(Cl)/NaCl/Hg/Hg_2SO_4$.

The diffusion test started when the inlet valve was opened. During the test the temperature and the level of the fluid in the inlet reservoir were controlled. To obtain an homogenizable situation (see Equation (39) and the comments that follow), the test has to last a sufficiently long time. Therefore, the time of the concentration measurement was chosen to be 143 days. The solution in the left reservoir was regularly mixed, with the inlet to the model kept closed (for several minutes, to be compared to the experiment duration, 143 days). Upon completion of the test, final reservoir samples were taken to determine the final solute concentration. The diffusion test was performed at an average temperature 18.66°C ± 1.01°C (143 measurements). To prevent the bacterial growth, silver scobs were used.

5.3. TEST RESULTS

The following experimental results were obtained

- From the analysis of cations Na^+ we obtained

$$c_{00} = c(t = 0) = 894.11\,\mathrm{mg\,NaCl/dm^3} \pm 23\,\mathrm{mg}(27\text{ samples}),$$
$$c_t = c(t = 143\text{ days}) = 860.76\,\mathrm{mg\,NaCl/dm^3} \pm 26\,\mathrm{mg}(21\text{ samples}).$$

- The analysis of anions Cl^- yielded

$$c_{00} = c(t = 0) = 1042.02\,\mathrm{mg\,NaCl/dm^3}\ (1\text{ sample}),$$

$$c_t = c(t = 143\text{ days}) = 989.56\,\text{mg NaCl}/\text{dm}^3 \text{ (1 sample)}.$$

5.4. DATA ANALYSIS

After opening the inlet valve at $t = 0$, mass transport of chemical constituents occurs by molecular diffusion from the reservoir into the porous medium model. It results in a decrease in the concentration in the reservoir as function of time. This process is described by Equation (24) with the following initial and boundary conditions

$$c(0, 0) = c_{00}, \tag{26}$$

$$c(0, X) = 0, \tag{27}$$

$$\frac{\partial c}{\partial X}(t, L) = 0, \tag{28}$$

$$V\frac{\partial c}{\partial t} = D_n^{\text{eff}}\frac{\partial c}{\partial X}S \quad \text{at } X = 0. \tag{29}$$

Equation (26) is the solute balance of the inlet reservoir in which ideal mixing is assumed. V is the volume of the liquid in the inlet reservoir. S is the volume of the pores in the period divided by the length of the period: it represents the macroscopic pore cross section. In the considered case $S = 501.3\,\text{mm}^2$.

The solution to the Problem (24), (26)-(29) can be approximated by the solution for the semi-infinite model $L = \infty$. This approximation is appropriate because at small time the influence of the sample end can be ignored. In this case the condition (28) is replaced by Equation (30)

$$c(\infty, t) = 0. \tag{30}$$

The solution to the Problem (24), (26)-(27), (29)-(30) is as follows

$$\frac{c(T^*, X^*)}{c_{00}} = \mathrm{e}^{T^* + X^*} \ \operatorname{erfc}\left[\sqrt{T^*} + \frac{X^*}{\sqrt{4T^*}}\right], \tag{31}$$

where the dimensionless distance X^* and the dimensionless time T^* are expressed by

$$X^* = X\frac{S}{V} \tag{32}$$

and

$$T^* = \frac{S^2}{V^2}D_n^{\text{eff}}t. \tag{33}$$

For $X^* = 0$ we have

$$\frac{c(T^*)}{c_{00}} = \mathrm{e}^{T^*} \operatorname{erfc} \sqrt{T^*}. \tag{34}$$

Figures 10 and 11 show a zoom of the function $f(T^*) = \mathrm{e}^{T^*} \operatorname{erfc} \sqrt{T^*}$ for small values of in the range of interest. This solution can be applied to analyse the results of the performed diffusion test. We proceed as follows. The final experimental value of the dimensionless concentration is used to obtain the corresponding dimensionless time T^* from Figures 10 and 11. Then, the determined value of T^*, together with the final test time $t_{\text{test}} = 143 \times 24 \times 3600\,\text{s}$ are introduced into relation (33), to get the effective diffusion coefficient.

- The analysis of cations Na^+ yields

$$\frac{c(T^*)}{c_{00}} = \frac{860.76}{894.11} = 0.9627 \quad \text{gives} \;\; T^* = 0.00116 \quad (\text{see Figure 10}).$$

Then, the effective diffusion coefficient is calculated

$$D_n^{\text{eff}} = \frac{T^* V^2}{S^2 t} = \frac{0.00116 \times 10^6}{(5.013)^2 143 \times 24 \times 3600} = 3.74 \times 10^{-6} \frac{\text{cm}^2}{\text{s}}. \tag{35}$$

- The analysis of anions Cl^- yields

$$\frac{c(T^*)}{c_{00}} = \frac{989.56}{1042.02} = 0.9497 \quad \text{gives} \;\; T^* = 0.002155 \quad (\text{see Figure 11}).$$

In this case the effective diffusion coefficient is

$$D_n^{\text{eff}} = \frac{0.002155 \times 10^6}{(5.013)^2 143 \times 24 \times 3600} = 6.94 \times 10^{-6} \frac{\text{cm}^2}{\text{s}}. \tag{36}$$

The two values of the effective diffusion coefficient can be averaged by considering the mass flux of NaCl as equal to the sum of mass fluxes of Na^+ and Cl^-. We obtain

$$D_n^{\text{eff, av}} = 5 \times 10^{-6}\,\text{cm}^2/\text{s}. \tag{37}$$

This value is in a good agreement with the numerical result (23).

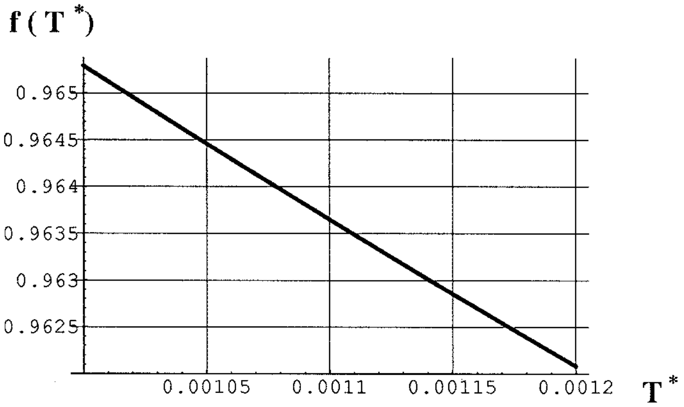

Figure 10. Zoom of the function $f(T^*)$ for small values of T^*.

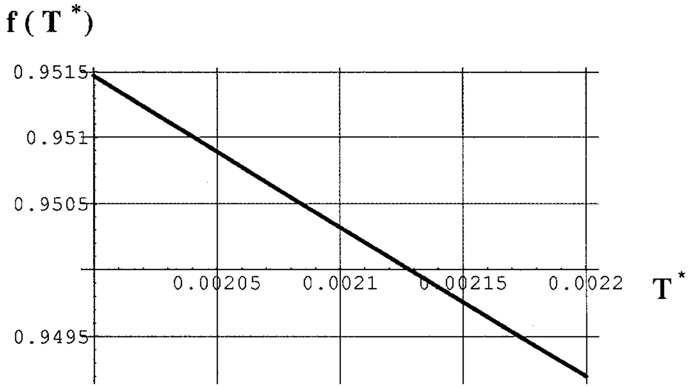

Figure 11. Zoom of the function $f(T^*)$ for small values of T^*.

5.5. VALIDITY OF THE APPROXIMATE ANALYTICAL SOLUTION

The validity of the approximate solution (34) can be checked by calculating the characteristic time of the diffusion test and by comparing it with the time duration of the test. The characteristic time of the diffusion test is given by

$$t_c = \frac{L^2}{D_n^{\text{eff}}} \approx \frac{90^2}{5.22 \times 10^{-6}} \approx 1.5 \times 10^9\,\text{s}. \tag{38}$$

As it can be seen, the time of the test $t_{\text{test}} = 143\,\text{days} = 1.23 \times 10^7\,\text{s}$ is small with respect to $t_c = 1.5 \times 10^9$. Therefore, the approximation (34) is appropriate to interpret the results of the experiment.

6. Discussion

The comparison between the obtained results indicates that there exists a good agreement between the theoretical and experimentally determined effective diffusion coefficient. Nevertheless, some discrepancy between the two values, namely 5.22×10^{-6} cm^2/s and 5×10^{-6} cm^2/s is noticed. There are many possible sources of errors in the experimental estimation of the effective diffusion coefficient, like

- temperature variations $(\pm 1^0)$,
- modifications of the pore geometry due to the utilization of glue to make the model leak-proof and to the imperfections of the model realization (the volume estimated experimentally was 434 cm^3 instead of 451 cm^3),
- presence of parasite phenomena, like anion adsorption of Cl$^-$,
- bacterial activity. Biochemical corrosion appeared to be an important problem during the first test trial when the model was made of duraluminium.
- errors related to collection of solution samples,
- precision of chemical analyses,
- error in the estimation of the molecular diffusion coefficient D for NaCl.

Another origin of error may be related to the limit conditions of the homogenizability of the problem considered. To analyze this aspect of the problem let us recall the definition of the homogenization parameter ε introduced in Boutin and Auriault (1990). In our case it is written

$$\varepsilon = l \frac{|\partial c/\partial x|}{c_{00}}. \tag{39}$$

The definition (39) was used to calculate ε as a function of the space variable for the final time of the experiment $t_{\text{test}} = 1.23 \times 10^7$ s, i.e. $T^* = 1.62 \times 10^{-3}$, Figure 12. In Figure 13 the concentration profile for the same time is presented. It can be seen that at time t_{test} diffusion occurs in the part of the model from 0 to 0.15 (that corresponds to 30 cm or 33 periods, approximately). Again it confirms the validity of the approximate solution (34). However, at $X = 0$, i.e. at the reservoir inlet, $\varepsilon \approx 0.13$ that makes the measurements conditions slightly over the generally accepted upper limit, which is usually assumed to be 0.1 for homogenizable situations. This may disturb the result.

It should be pointed out that in general the homogenization analysis introduces boundary layers of the width equivalent to one or two periods along the external boundaries of the porous medium. However, in our particular problem such a boundary layer does not exist and we have at $X = 0$ the concentration $c = c_{\text{reservoir}} = \text{cst}$ all along the macroscopic boundary.

The obtained results can also be interpreted in terms of the tortuosity factor τ, (Bear and Verruijt, 1987), that expresses the effect of the microscopic configuration of the pores on the effective diffusion coefficient. By following the definition in

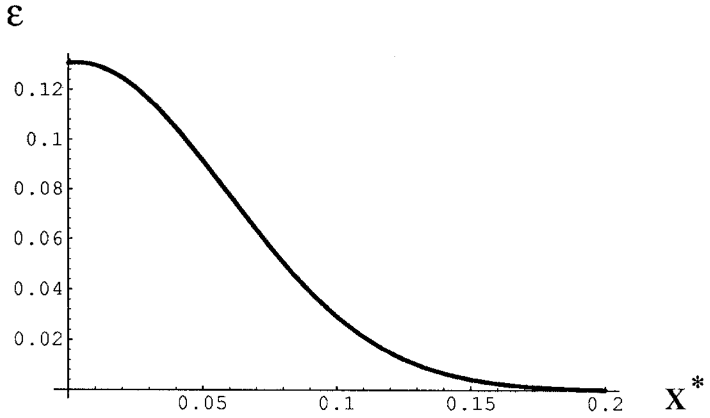

Figure 12. Variations of ε with X^* for $t_{\text{test}} = 1.23 \times 10^7$ s.

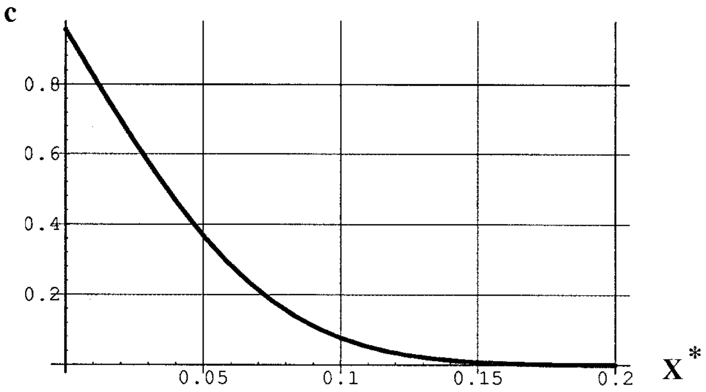

Figure 13. Concentration profile for $t_{\text{test}} = 1.23 \times 10^7$ s.

Bear and Verruijt (1987), we obtain the general expression for the tortuosity tensor τ in the case when the molecular diffusion tensor is assumed as isotropic

$$\tau_{ij} = \frac{1}{|\Omega|} \int_{\Omega_l} \left(I_{ij} + \frac{\partial \chi_j^*}{\partial y_i} \right) \mathrm{d}\Omega. \tag{40}$$

In our case we obtain

$$\tau_{11\,\text{num}} = 0.3833 \quad \text{and} \quad \tau_{11\,\text{exp}} = 0.3671. \tag{41}$$

These two values are rather close each to other; the experimental value slightly underestimates the value of the tortuosity factor.

7. Conclusions

In the paper an example of the application of the homogenization approach to calculate the effective diffusion coefficient for one-dimensional periodic porous medium, together with the experimental verification of the theoretical result was presented. To the authors best knowledge such a comparison has never been made before. The existing discrepancy between the results proves that the investigations toward better understanding and description of the diffusion phenomenon should be continued.

For real porous media it is practically impossible to solve the local boundary value problems to obtain the theoretical value of the effective diffusion coefficient, because of the complex pore geometry. Simplified formula based on the porosity of the medium proved to be inadequate in the case of anisotropic systems (like the one considered), for which the details of the geometry play an essential role. Therefore, very often experiment is the only available method of prediction of the effective diffusion coefficient.

Finally, the experimental effort has to be emphasized. Although very simple in conception, the diffusion test was found to be very difficult to carry out and several trial tests were necessary in order to elaborate the final test procedure. It is pointed out that the diffusion parameter identification test should be programmed in a way to ensure the homogenizability condition to be satisfied. It practically means long duration of a test and thus problems to maintain the constant test conditions (bacteria growth, pH variations, etc.). If the homogenizability condition is not met, the obtained diffusion coefficient is not an intrinsic parameter and can not be applied to field conditions.

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