An Indirect Approach for Correlation
of Permeability and Diffusion Coefficients

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Abstract. Diffusion tests in porous media are quite sensitive and long lasting procedures compared to permeability tests, which are usually more reliable and of shorter duration. Both diffusion and advection phenomena are dependent on the tortuosity of the material tested. A relevant question is to know whether it is possible to correlate permeability tortuosity τ_p and diffusion tortuosity τ_d. Several diffusion and permeability tests have been performed on non-uniform sand specimens having different grain size distribution. For each specimen, both the permeability and diffusion coefficients have been measured and two tortuosity factors (permeability and diffusion) have been back calculated. A theoretical model has been proposed to estimate τ_d from τ_p for a non-uniform granular material. The maximum particle diameter d_{max} is used to determine the maximum hydraulic diameter d_{h-max} using the Hydraulic Radius Theory (HRT) for a 3D arrangement of spheres of same diameter d_{max}. Then, a filling factor α is applied to d_{h-max} in order to capture the fact that smaller grains tend to fill the voids present in between the bigger particles. The filling factor is based on the coefficient of uniformity C_u. Relatively good results are obtained so that this model allows estimating the diffusion properties from a simple permeability test rapidly and at a fraction of the diffusion test cost.

Introduction

The tortuosity factor appears in the different theoretical transport equations (permeability, diffusion and electrical conductivity) as a fitting parameter to account for the ratio between "free" and effective transport coefficients. In the last few years, a number of authors have reviewed this concept in detail [1-3]. Historically, the tortuosity factor was firstly introduced by Carman [4] to account for the sinuosity in the flow path in porous media described as a bundle of sinuous capillary tubes with a uniform cross section of diameter d_h and length $L_e>L$ (The effective length and the sample length, respectively). Accordingly, Carman [4] defined tortuosity as

$$\tau = \left(\frac{L}{L_e}\right)^2 .$$
(1)

As a result of this definition, τ would always be less than unity. The determination of τ from this definition is often cumbersome since the effective length L_e of the fluid flow is not a measurable quantity. To overcome this difficulty, the tortuosity factor is quantified experimentally from either the electrical conductivity measurements as advised by Carman [4] or from the diffusion measurements as recommended by Bear [5], Olsen and Kemper [6] and Garrouch et al. [7]. This is practically done by noting the difference in the transport coefficient values, conductivity or

diffusivity, with and without the porous media according to Eq. 2 and Eq. 3, respectively. By doing so, the retardation influence of the porous media is captured, and hence the tortuosity factor is determined.

$$\sigma_{eff} = \sigma_0 n_e \tau_c .$$ (2)

$$D_{eff} = D_0 n_e \tau_d .$$ (3)

Here, σ and D are the electrical conductivity [S/m] and the diffusion coefficient [m^2/sec], respectively. n_e is the experimental total porosity [m^3/m^3]. τ_c and τ_d represent the conductivity tortuosity and diffusion tortuosity, respectively. The subscripts *eff* and *o* stand for the measurements with and without porous media, respectively.

The convenience of using the tortuosity from the diffusion or the conductivity measurements to substitute for each other has been demonstrated by many authors. For instance, Garrouch et al. [7] have pointed out that the tortuosity in sandstone measured from either diffusion or electrical conductivity measurements converged approximately to the same value, where they attributed the deviation to the pore wall effect, since the electrical charge in porous media does not experience adhesion on the slip side whereas diffusing gases do. This good agreement between tortuosity from diffusion and conductivity measurements have been also obtained by Latour et al [8] and Barrande et al. [9]. The reason for the agreement in the tortuosity from diffusion and conductivity measurements is attributed to the strong analogy between the two phenomena. Indeed, both of them can be described by the Laplace equation [10] and, they are related through the Nernst-Einstein equation [9].

However, to the best of our knowledge, no work has been devoted to quantify the tortuosity factor from permeability measurements. Maybe one of the major reasons of this is the lack of a free permeability definition (permeability without porous media) as in the case of diffusion and electrical conductivity [9] and the fact that the phenomena (advection and diffusion) are different. Thus, no study is available to compare the tortuosity from permeability with the tortuosity from either the diffusion or the electrical conductivity measurements.

The objectives of this study are two fold: firstly, to develop a model to estimate the free permeability and thus calculate the permeability tortuosity from permeability measurements. Secondly, to compare the tortuosity measured from both the permeability and the diffusion measurements and thus to develop a model to estimate the diffusion coefficient from the simple permeability test.

Experimental Facilities

Materials. The specimens were made from sand (0.150-4.75 mm) supplied by the Specialized Gravel Services, Australia. The source solution is made of potassium bromide (KBr) of analytical grade (99.8%) supplied by Sigma-Aldrich Pty. Ltd (Australia). It was dried for 5 hours at 45^{0}C before using in the preparation of solutions [11]. Distilled deionized water obtained from the Milli-Q Plus system (Millipore, Milford USA) with electrical resistance [18.2 M.Ohm.cm] was used as a collector solution in diffusion measurement and as a seeping fluid in permeability measurement. The prepared solutions were kept in a temperature control box before using in the experiments to equilibrate with the desired test temperature.

Sample Preparation. The sand samples were carefully washed with distilled deionized water in order to purify them from any chemical impurities. The washed sand was then dried in the oven at 105 °C for 48 hours. A mixture of sand with distilled deionized water at a given molding water content was then compacted in the test tube, of 3.8 cm in diameter, between a geo-textile disk (ProFab AS140- Global Synthetics, Australia) and a perforated Perspex disk at each side by either an adapted Proctor method in three layers with 25 tamps per layer to the required thickness within

the test tube or in one layer by applying a static or hydrostatic load in the specimen for a certain period of time until the desired level of compaction was achieved [12]. The test specimen was then clamped on both sides in order to avoid disturbing the sample and to ensure its dimensional stability throughout the experimental duration. A portion of the molding sand mixture was then dried in the oven for 24 hours to find the molding water content, which was needed for the measurement of other physical properties as bulk and dry densities and porosity [13].

Permeability Test. A permeameter allowing both constant head and falling head tests has been designed in order to measure the permeability for sand assemblies. This device had to be designed to suit the dimensions of tested samples and the relatively high permeability, of the order of 10^{-6}-10^{-3} [m/sec], limit the use of pressure controllers as advised by Klute and Direksen [14].

   During the tests, attention was paid to avoid unsaturated flow through the specimen as suggested by [15]. The flow through the apparatus was controlled by using a polyethylene stopcock which connects the basement of the drainage system with the drainage pipe.

   The permeability tests were conducted ensuring full saturation of the sample and using deionized water. The permeability was calculated by applying Darcy's law [13] in Eq. 4.

$$K = \frac{Q}{A.n_e.I} \cdot$$

(4)

where K is the permeability [m/sec], I is the hydraulic gradient [m], Q is the flow rate [m^3/sec], A is the cross sectional area of sample [m^2].

Diffusion Test. The diffusion coefficient was measured based on the so-called diaphragm cell set-up. The designed apparatus is shown graphically in Fig. 1. It consists of two containers namely, the source (tagged with chemical ions) and the collector (initially free of chemical ions). The containers were covered by removable lids to hinder the evaporation of solutions and to facilitate the liquid sampling. The source and the collector containers were linked together by a horizontal test tube. The test tube itself and the two containers were made of Perspex. The volume of source and collector solutions was 2000 ml. The solutions in both containers, which were kept homogeneous with the aid of a continuous magnetic stirring, were maintained at the same level to avoid the advective flux of ions due to the hydrostatic pressure. The diffusion experiments were performed in a temperature control box (30±0.1^{0}C) to avoid any temperature effects. Special arrangements allow the forming of the specimen into the Perspex tube and testing it without unmounting it firstly in the permeameter and then in the diffusion set up.
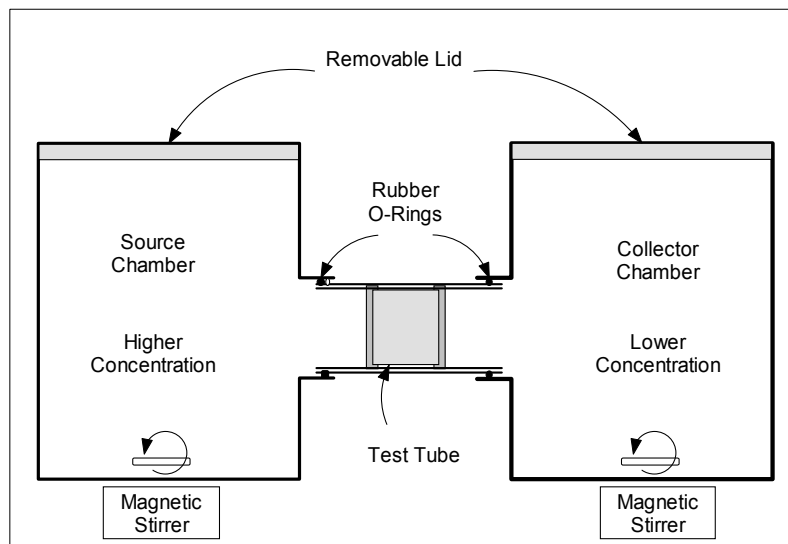

Fig. 1: Diffusion apparatus.

The ionic flux from the source to the collector containers through the porous specimen was estimated by pipetting a number of liquid samples (0.1 ml with a micropipette) from both containers at successive time intervals. The liquid samples concentrations were obtained by an Ion-Chromatography unit (ICS-3000 RFIC^{TM} system, Dionex Corporation-USA).

The diffusion coefficient was then obtained by solving the 1D diffusion flux in porous media formula, which is given by Fick's second law [16] in Eq. 5, with the quasi steady-state initial and boundary conditions shown in Eqs. 6-8.

$$\frac{\delta c}{\delta t} = D_e \frac{\partial^2 c}{\partial x^2} .$$ (5)

$$c = c_{c_o}, \; c = c_o, L > x > 0, \; t = 0 .$$ (6)

$$c = c_s, \; An_e D_e \frac{\partial c}{\partial x} = V_s \frac{\partial c_s}{\partial t} , \; x = 0, t > 0 .$$ (7)

$$c = c_c, \; An_e D_e \frac{\partial c}{\partial x} = -V_c \frac{\partial c_c}{\partial t} , \; x = L, t > 0 .$$ (8)

where D_e is the diffusion coefficient [m^2/sec]. $\left(\frac{\partial c}{\partial x}\right)$ is the concentration gradient across the sample [mol/sec L, g/ sec L]. V_s and V_c are the solution volume in source and collector compartments, respectively [m^3], $\left(\frac{\partial c_s}{\partial t}\right)$ and $\left(\frac{\partial c_c}{\partial t}\right)$ are the rate of concentration change in source and collector compartments, respectively [mol/sec L, g/ sec L].

The boundary conditions described in Eq. 7 and Eq. 8 assume that the rate change of solute diffusion in both source and collector compartments respectively are equal to the flux rate of chemical species from the porous media to the compartments. Practically that could be achieved after the system reaches the quasi steady-state condition. In such a condition, the ratio between the temporal concentration gradient measured at such time instant upon the required time to achieve a linear concentration profile across the test specimen and the corresponding rate of concentration evolution in collector cell stays constant.

Estimation of Free Permeability

In this study, an equation similar to Eq. 3 is defined in order to estimate the permeability tortuosity factor:

$$K_{eff} = K_0 \, n_e \, \tau_p .$$ (9)

where K_{eff} stands for the effective permeability (with porous media) and K_0 represents the free permeability (without porous media), n_e is the porosity and τ_p is the permeability tortuosity factor. Estimating the free permeability is not trivial and one existing approach is presented in the following section.

Hydraulic Radius Theory. A model for estimating the permeability in porous media according to the Carman-Kozeny equation or the so-called hydraulic radius theory *HRT*, where the porous media is described as a bundle of sinuous capillary tubes with a uniform cross section of diameter d$_h$ and length L$_e$ [17] is given as

$$K_{eff} = \frac{\rho \, g \, d_h^2 \, n_e \, \tau_p}{16 \, \varsigma \, \mu} \; . \tag{10}$$

Here, K_{eff} is the permeability of the porous media [m/sec], ρ is the fluid density [kg/m^3], g is the gravitational acceleration [9.81 m/sec^2], d_h is the mean hydraulic diameter of capillaries [m], ς is a dimensionless shape factor for the capillary tube equals 2-3 for a granular material [18], μ is the dynamic viscosity [N.s/m^2] and τ_p is the permeability tortuosity factor. Eq. 10 can be rewritten as Eq. 9 by defining K_0 as:

$$K_0 = \frac{\rho g \, d_h^2}{16 \varsigma \, \mu} \; . \tag{11}$$

This formulation relies on the idealization of the porous medium as a collection of uniform capillary tubes, which tends to limit its use to uniform materials, which is more than unlikely when considering natural granular materials. The impossibility to use this formulation for non uniform materials is discussed in the results section.

A Simple Model for the Free Permeability of Non Uniform Granular Materials. In a non uniform material, the smallest particles tend to fill the voids existing between the biggest particles. The model for the non uniform granular materials is based on the idea of the *HRT* but incorporating the idea of "filling" by the smallest particles. The hydraulic diameter d_h is proposed to be a combination of the biggest particles (of diameter d_{max}) and of a filling function α representing the filling effect of the smallest particles:

$$d_h = d_{h-\max} \, \alpha \; . \tag{12}$$

where, d_{h-max} is the hydraulic diameter based on the maximum grain size present in the sample of diameter d_{max} [m] and α is a function accounts for the filling effect of the small grains for the void space between the large ones. The hydraulic diameter d_{h-max} is then estimated from the *HRT* [2] as

$$d_{h-\max} = \frac{4 n_e}{S_s (1 - n_e)} \; . \tag{13}$$

where S_s denotes the specific surface [m^2/m^3]. The specific surface is not trivial to measure experimentally for a real material so that, the porous media is assumed to consist in 3D Simple Cubic *3D-SC* model of equal spheres size of diameter d_{max} [m] (Fig. 2), for which the specific surface S_s can be estimated as

$$S_s = \frac{8.459}{d_{\max}} \; . \tag{14}$$

Fig. 2: 3D equal spheres size in a Simple Cubic arrangement.

To be consistent, the porosity in Eq. 13 is taken as that of the simple cubic arrangement n_m, which has been found to be 0.476. Combining Eqs.11-14 results in:

$$K_0 = \frac{\rho g \alpha^2 d^2_{max}}{86.72 \varsigma \mu}$$

(15)

Results and Discussion

Calibration of Filling Function α. For the permeability model to be used in predicting τ_d values, the filling function α needs to be calibrated. A number of permeability and diffusion tests on various samples having different grains size distributions have been used. The samples are chosen to capture the natural variation of uniformity coefficient C_u in real materials. The filling function has been calibrated considering that diffusion and permeability tortuosity factors were equal and then using the following calculation:

$$\alpha = \sqrt{\frac{86.72 \varsigma \mu K_{eff}}{\rho g n_e \tau_d d^2_{max}}}$$

(16)

The shape factor ς is taken as 2.5 as advised by [18] for a granular material. The gravitational acceleration g is given as 9.81 [m/sec^2]. The fluid density ρ and the dynamic viscosity μ are taken as 997 [kg/m^3] and 8.91×10^{-4} [N.s/m^2], respectively for the water at 30 ^{0}C [19]. The tortuosity from the diffusion measurements τ_d is calculated from Eq. 3 where D_0 is given as 2.118 [×10^{-9} m^2/sec] for a KBr solution with 0.1-0.3 [M] in concentration and 30 ^{0}C in temperature [20]. The parameters for test specimens are given in Table 1.

Table 1: Tests parameters for α calibration.

Sample No.	Grain size [10^{-3} m]	C_u	n_e [m^3/m^3]
K1	0.212-0.150	1.198	0.39
K2	0.6-0.425	1.203	0.415
K3	0.3-0.212	1.204	0.417
K4	1.18-0.6	1.441	0.39
K5	2.36-1.18	1.455	0.329
K6	4.75-1.18	1.530	0.331
K7	4.75-0.212	2.160	0.244
K8	4.75-0.6	2.950	0.205
K9	4.75-0.3	4.150	0.159

The obtained filling function values from those test set-ups are then plotted in Fig. 3 as a function of the coefficient of uniformity C_u.

As shown in Fig. 3, an exponential relationship with a fairly good correlation coefficient (R^2=0.85) has been obtained between α and C_u. As demonstrated in Fig. 3, the α values decline sharply from its maximum theoretical value (α=1) for a perfectly uniform material (C_u=1) until it reaches its minimum value (α=0.07) at C_u equals 2. Beyond this C_u value, the filling function α maintains a constant value with the increase of sample non-uniformity. The resultant formula is given in Eq. 20. It is used as a benchmark to estimate the filling function α in the permeability model.

$$\alpha = 0.07 + 108.78\, e^{-4.76 C_u}. \tag{20}$$

The workability of the developed methodology to estimate τ_d based on permeability measurement is tested in the next section.
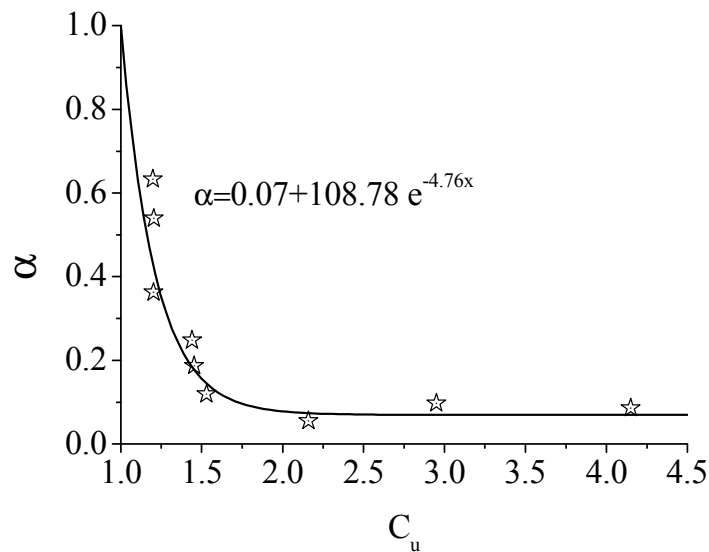

Fig. 3: Correlation of the filling factor α with the uniformity coefficient.

Prediction. In order to assure the capability of the proposed permeability model in estimating τ_d, a series of permeability and diffusion tests have been arranged on a variety of test specimens with different grain size distribution from those used in calibration of α. The required parameters for those test set-ups are given in Table 2.

Table 2: Tests parameters for validation of permeability model.

Sample No.	Grain size [10^{-3} m]	C_u	n_e [m^3/m^3]
K10	0.425-0.3	1.2	0.40
K11	4.75-2.36	1.460	0.319
K12	4.75-1.18	1.702	0.346
K13	4.75-1.18	1.895	0.329
K14	4.75-1.18	2	0.329
K15	4.75-1.18	2.059	0.349
K16	4.75-0.425	3.5	0.292

The diffusion tortuosity for each test set-up is then twice calculated, one from the permeability measurements according to Eq. 21 and the other from the diffusion measurements based on Eq. 22.

$$Estimated \; \tau_d = \tau_p = \frac{K_{eff}}{K_0 \, n_e} \,. \tag{21}$$

$$Measured \; \tau_d = \frac{D_{eff}}{D_0 \, n_e} \,. \tag{22}$$

The estimated tortuosity values from the proposed permeability model which are plotted as a function of C_u in Fig. 4 are then compared against the corresponding directly measured ones from the diffusion tests. The comparison is shown in Fig. 5.
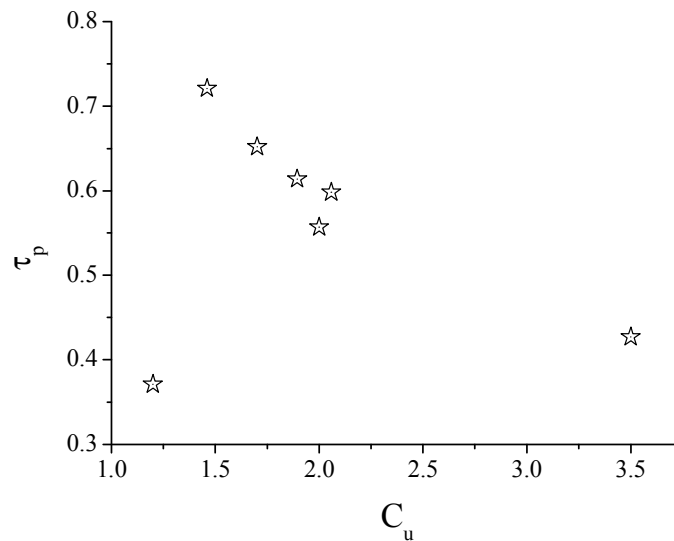

Fig. 4: Permeability tortuosity τ_p obtained from the modified *HRT* permeability model as a function of uniformity coefficient C_u.
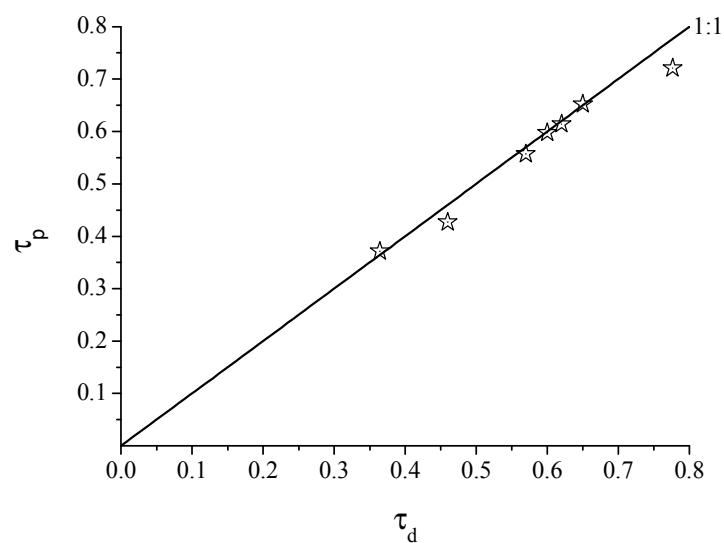

Fig. 5: Comparison between the permeability tortuosity τ_p obtained from the model and diffusion tortuosity τ_d obtained from the diffusion tests.

It is clear from Fig. 5 that the tortuosity factors calculated from permeability measurements τ_p agree well with those calculated from diffusion measurements τ_d with almost negligible difference. The achievable good agreement is not surprising, thus the tortuosity in the diffusion problem which is defined as a retardation factor to lump the fluidity, the anion exclusion and the geometrical restriction effects [21] is reduced for the granular materials to the geometrical definition as for the permeability problem. Since, the influence of both the fluidity and the anion exclusion becomes prominent in case of very fine pore channels as for clay and concrete [21].

However, the slight differences between τ_p and τ_d could be attributed to the fact that the two transport phenomena (advection and diffusion) are different. Moreover, different non-avoidable experimental errors might be also blamed for such difference. To show the significance of incorporating the filling effect of the small grains in the accuracy of the permeability model for the non uniform materials, the diffusion coefficients for test setups in Table 2 are twice estimated, one based on the *HRT* (without filling effect) where, d_h is assumed to equal $d_{h\text{-}50}$ (the porous media consist in the Cubic *3D-SC* model of equal spheres size of diameter d_{50}). and the others from modified *HRT* (with filling effect) as described before. The comparison between the directly measured diffusion coefficients and the estimated ones from the permeability measurements for the two assumptions from the *HRT* and the modified *HRT* for the test set-ups in Table 2 are shown in Fig. 6 and Fig.7, respectively.
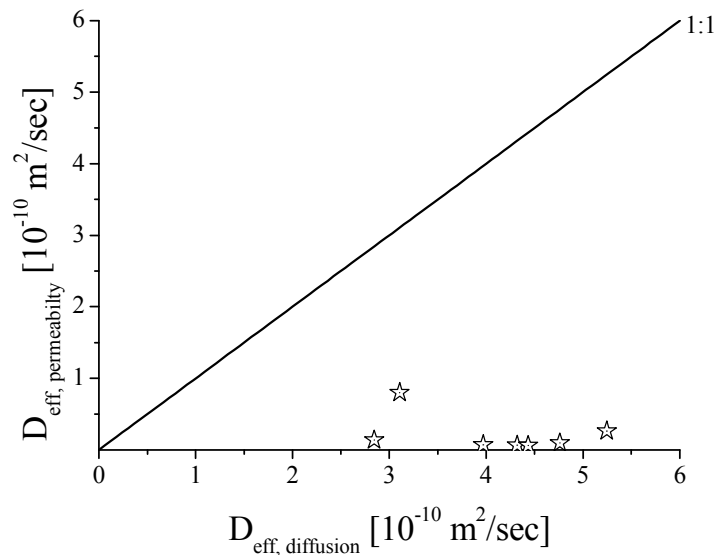

Fig. 6: Comparison between diffusion coefficients from diffusion tests and estimated from permeability measurements (*HRT*).
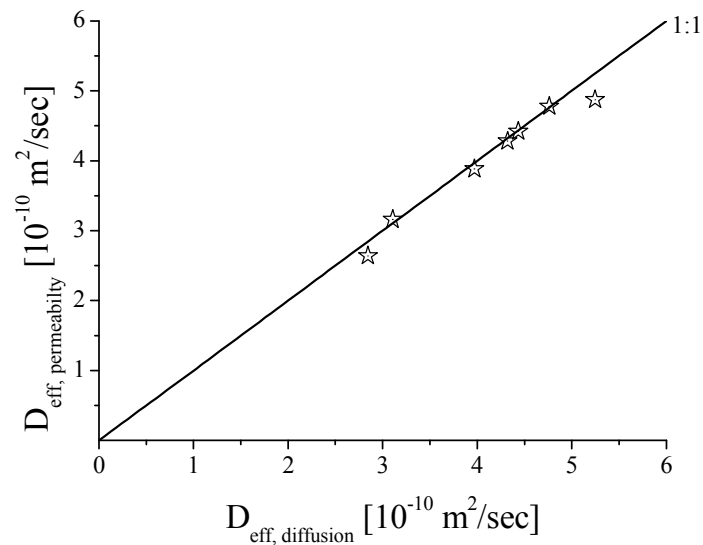
Fig. 7: Comparison between diffusion coefficients from diffusion tests and estimated from permeability measurements (modified *HRT*).

The results in Fig. 6 and 7 demonstrate the creditability of the developed permeability methodology to determine the diffusion coefficient based on the modified *HRT*. Thus, huge scattering is obtained from the simple *HRT* model in Fig. 6 whereas fairly good estimation for the diffusion coefficients from the modified *HRT* in Fig. 7 obtained with a difference of about (0.3-7%) from those determined from the directly measured diffusion coefficients.

Conclusion

Measuring the diffusion coefficients of granular materials is a long lasting and precise experimental procedure whereas performing permeability tests is more simple and reliable. A new indirect method to determine the diffusion properties in non-uniform sand from permeability measurements is presented. It is based on the idea that, in natural non-uniform sand, the smallest particles would fill the gaps existing between the largest particles. A filling function α is then defined and calibrated on the basis of a calibration set of tests. This filling function is applied to reduce the maximal hydraulic diameter obtained from the diameter of the biggest particles. Reasonably good agreement was obtained between the measured diffusion coefficients and the estimated diffusion coefficients (from permeability tests). These results suggest that the model could be used for an easy and reliable estimate of the diffusion properties of a natural non-uniform granular material. As a result, the costly and time consuming diffusion properties could be obtained efficiently with less time and cost with the aid of permeability measurements.

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Diffusion in Solids and Liquids IV

**An Indirect Approach for Correlation
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