

IMAGE MODELING OF MIXED GRANULAR POROUS MEDIA

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Two-dimensional image modeling of binary and ternary mixed porous media was used to study the effect of porosity and tortuosity on effective diffusion coefficient and permeability were separated. Different volume fractions of large and small particles in the mixtures as well as different particle size ratio were investigated. The following results were obtained: 1). The porosity changes with variation of the volume fraction of large particles in the mixture. The function of the porosity vs. volume fraction of large particles passes through a minimum. 2). The dependence of tortuosity on the volume fraction of large particles has a maximum, which does not coincide with the minimum value of the porosity. 3). The introduction in the binary mixture of a third fraction of particles with a much smaller diameter led to a dramatic decrease of porosity. For a volume fraction of smaller particles as low as 0.05 - 0.1 in the total volume of particles the porosity was 20 - 30% of the corresponding mono-sized porous media. This deviation increased with the increase in the particle size ratio. 4). This analysis shows that the characterization of a mixed bed must take in account other properties besides particle size. Different beds with the same equivalent particle diameter can have different porosity or tortuosity. 5). The ratio ϵ/T , a term included both in the permeability and effective diffusivity expressions, also passes through a minimum. Therefore, a change in the volume fraction of large particles in the binary mixture may give rise to a 70% decrease in the effective diffusivity of the porous medium and up to 85% decrease for ternary mixtures. This effect is more significant in the case of permeability.

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INTRODUCTION

Porous media play an important role in nature and technology. There are several models and approaches that describe porous media properties and associated mass transfer phenomena (Bear, 1972; Dullien, 1975, and Suzuki, 1990). In general, the major porous media properties are expressed in

two parameters - the permeability coefficient (flow phenomena) and the effective diffusion coefficient (mass transfer phenomena). Both coefficients include two main characteristics of porous media: porosity, ϵ , and tortuosity, T .

The flow of fluid through a porous medium may be described by the Kozeny-Carman model (Bear, 1972):

$$u = k \frac{\Delta p}{\mu L} \quad (1)$$

where u is the fluid flow velocity; k , the permeability; Δp , the pressure drop; μ , the fluid viscosity, and L , the media thickness. The Kozeny coefficient, K , may be expressed as

$$K = K_0 T^2 \quad (2)$$

where K_0 is a constant that equals 2 in most cases. From equation (1) and (2), the permeability k is given as:

$$k = \frac{\epsilon^3 d_s^2}{36 K (1 - \epsilon)^2} = \left(\frac{\epsilon}{T} \right)^2 \frac{\epsilon \cdot d}{36 (1 - \epsilon)^2 K_0} \quad (3)$$

where ϵ is the porosity, and d_s is the particle equivalent diameter.

Mass transfer phenomena depend on the effective diffusion coefficient as defined below

$$D_e = D_0 \frac{\epsilon}{T} \quad (4)$$

or

$$\eta = \frac{D_e}{D_0} = \frac{\epsilon}{T} \quad (5)$$

where D_e is the effective diffusion coefficient in porous media and D_0 is the diffusion coefficient in a bulk liquid.

As can be seen, mass transfer as well as flow phenomena depend on ϵ/T and $(\epsilon/T)^2$, respectively. However, tortuosity T is a function $T(\epsilon)$ of porosity (Bear, 1972; Dullien, 1975; Suzuki, 1990; McCune, et al., 1979). For granular mixed beds, both tortuosity and porosity are related to the volume fraction of different sized particles in

the mixture. A background for the description of the porosity of beds was developed and discussed in Yu, et al. (1996), Zou and Yu (1996), but the problem of the tortuosity relationship with porosity and particle size distribution remains actual for mixed granular beds. Permeability as well as effective diffusivity contain ϵ and T in the form of ratio ϵ/T , as was mentioned earlier. The relationship between porosity and tortuosity is the subject of this work.

Since physical modeling of the tortuosity in mixed beds is rather complicated, the objective of this work is: 1) to solve two-dimensional modeling of binary and ternary beds, 2) to estimate the lower bound for tortuosity and 3) to determine the influence of large particle volume fraction in the mixture on tortuosity, porosity and ratio ϵ/T .

PREVIOUS STUDIES

The porosity, ϵ , of mixed particle beds has been described by experimental, geometrical and statistical approaches for randomized porous media, etc. (Gotoh, et al., 1982; Hulewicz, 1987; Kuramae, 1982; Lin and Slattery, 1982; MacDonald, et al., 1991; Macé and Wei, 1991; Ouchiyama and Tanaka, 1981; Ouchiyama and Tanaka, 1984; Suzuki, et al., 1981; Yu and Standish, 1991). In many cases the results depended on the packing method applied.

The effect of packing method on the randomness of uniform discs packing was investigated by Zhang et al. (1996). Three simulation algorithms gave the following packing density ϕ : 1) for random sequential adsorption, $\phi = 0.543$, 2) for random packing under gravity, $\phi = 0.840$ and 3) for Mason packing, $\phi = 0.906$.

A spherical uniform particle computer simulation of weight distribution in beds on the bottom of a container was done by Gotoh et al. (1982) for different initial particle position. An improved Monte Carlo computer simulation procedure, described by Tory et al. (1973) was used. According to the procedure, when a particle reached contact with some of the particles in the surface of the bed, the particle rolls on the border of this packed particle until contact is established with another particle. The authors pointed out that from the microscopic point of view the bed structure was such that the load of each particle extended a long way out from the particle-feed position. The modified procedure of Tory et al. (1973) was used in three-dimensional simulation of random packings of uniform-sized spherical particles (for determining a coordination number, by Suzuki et al., 1981) as well as for two-dimensional sediments generation (Tassopoulos and Rosner, 1992).

Typical plots of two-dimensional porous media models generated in current work are shown in Figure 1 and will be discussed below. Here $n=D/d$; ϵ/ϵ_0 is the normalized porosity where ϵ_0 is the porosity of a monosized bed; T/T_0 is the normalized tortuosity where T_0 is the tortuosity of a monosized bed; η/η_0 is the normalized diffusivity where η_0 is the diffusivity of a monosized bed.

Abe and Hirose (1982) presented equations that predict the porosity dependence on the volume fraction of the large

particles in beds of binary mixtures. According to Abe and Hirose (1982) for binary mixture the dependence of porosity, ϵ , on volume fraction of large particles, x_D , is represented by equations 6 and 7. These functions form a curve with an intersection point which divided the dependence in two parts: part I is a left branch of the dependence of ϵ on x_D for mixtures enriched with small particles and part II is a right branch of the dependence for mixtures enriched with large particles. An example of this dependence is shown in Figure 2a, line (1). The point of intersection of left and right branches of the dependence corresponds to a mixture where the amount of large particles is enough to build up a support skeleton for the smaller particles. Porosity for both branches of the dependence may be calculated as follows.

- for the left branch of the dependence

$$\epsilon = 1 - \frac{1 - \epsilon_D}{(1 - x_D) + \alpha \cdot x_D(1 - \epsilon_D)} \quad (6)$$

where $\alpha = 1 + f_c \cdot (d/D)$; D is the large particle diameter in the mixture; d is the small particle diameter, and f_c is a coefficient and equal to unity for $d/D = 0.5$, 1.2 for $d/D = 0.25$ and 1.4 for $d/D = 0.125$. Porosity is defined as the porosity of monosized bed of small particles.

- for the right branch of the dependence the porosity defined by equation

$$\epsilon = 1 - \frac{1 - \epsilon_D}{x_D(1 + \beta_s \beta_c)^3} \quad (7)$$

where $\beta_s = (d/D)^n$, $\beta_c = \sqrt[3]{1 + \frac{1 - x_D}{x_D}} - 1$, $n = 1/2$, for

spherical particles and ϵ_0 is the porosity of monosized bed of large particles.

Assuming a porosity of 0.4 for monosized spherical particles beds then minimal porosity when $d/D \rightarrow 0$ corresponds to 0.16 when volume fraction of large particles in the mixture $x_D = 0.714$. This is the lower bound for porosity of a binary mixture of spherical particles by theoretical model of Abe and Hirose (1982). Ouchiyama and Tanaka (1981) give the comparison of some published data and numerical estimation. For a binary mixture of spherical particles it is shown that it is possible to reach in the case of $d/D \rightarrow 0$ a dense packing of a minimal porosity of about 0.14 in the region 0.72 ($= 0.375$).

However, the situation for tortuosity is less clear, because this parameter has an undefined character and is difficult to determine experimentally. Usually, tortuosity is calculated through measured porosity from experimental determination of effective diffusion or from Kozeny coefficient or by means of porous medium modeling.

Monte Carlo simulation methods of Knudsen diffusion in a spherical particle bed give a tortuosity variation of 2.5 - 5.0 for different models (Abbasi et al., 1983).

MacDonald et al. (1991) measured the permeability of ternary mixtures of spherical particles. Results were plotted on ternary diagrams for porosity and permeability. The tortuosity variation was not included. As MacDonald et al. (1991) pointed out, all the data, although scattered, clustered around the line representing the theoretical model. One of the possible reasons can be the dependence of tortuosity on porosity and as a result variation in permeability.

In modeling of liquid flow through porous media the tortuosity is sometimes used as a fixed value even in the case of wide range of porosity variations (Hulewicz, 1987).

Mocé and Wei (1991) used a model of random walks in a medium of random spheres and mentioned that tortuosity increased with increasing of volume fraction of spheres. On the other hand, tortuosity factor for diffusion in catalyst pellets calculated from experiments had a value of 6-8 according to Wang and Smith (1983). The authors pointed out that the tortuosity factor did not increase with the decrease in porosity between 0.677 and 0.569 for two pellets from granular particles with different size distribution.

Knudsen diffusion of non-adsorbing gas in binary mixtures of spheres was also considered (Wright et al., 1987). Microspheres in the size range 130-400 nm were used for modeling binary mixtures of particles with diameter ratios $d/D = 0.33$ and 0.44 . Experimental data were interpreted in terms of the dependence of the tortuosity on mean pore radius. For all diffusion measurements by means of "best" fit it was found that a single tortuosity value of 1.48 was sufficient. Narrower ranges in particle size and lack of data of the tortuosity vs. particle fractions in mixtures made these data difficult to interpret.

Catalyst pellets were simulated by packed beds of microporous ion exchange resin (bead size 0.47 mm) and inert glass particles of different size and shape (Klusáček and Schneider, 1981). Tortuosity was obtained by measuring experimentally the effect of internal diffusion on the rate of catalytic methanol dehydration. Both the tortuosity and porosity vary with the particle volume fraction and the particle size ratio in the mixture but the range of this variation for mixed beds needs to be estimated.

The tortuosity of ordered sphere packing was measured experimentally by Olague et al. (1988). It was pointed out that the theoretical tortuosity gives a lower bound for T since the direction of flow may be not aligned with the normal to the porous medium surface direction.

The complexity of the tortuosity behaviors led to different interpretations of the tortuosity (Bear, 1972; Dullien, 1975; Suzuki, 1990; Zhang and Bishop, 1994). Sometimes the definition of tortuosity applies to the path of some liquid or objects in a heterogeneous medium: this is for instance, the case of bubbles rise path in a liquid-solid fluidized bed (Tsuchiya and Furumoto, 1995). The tortuosity of the rise path was defined in this study as the ratio of the total distance to the net vertical distance traveled by a bubble.

It may be seen from the mentioned above data, that the tortuosity is a rather complex function of several factors: 1). Tortuosity is evident or latent in all models of mass transfer in porous media. 2). Tortuosity is not a physical constant and

depends first of all on other porous media characteristics like porosity, pore diameter, channel shape, etc. 3). Tortuosity often depends on processes occurring during mass transfer: porous media compressing or expanding, particles or macromolecules deposition inside pore channel, pore blocking phenomena, etc.

Moreover, if the porosity of mixed particle beds was investigated in the range of particle size ratio from 2 up to 10 (Abe and Hirose, 1982; Carta and Bauer, 1990; MacDonald, et al., 1991; Ouchiya and Tanaka, 1981; Suzuki, et al., 1981; Yu and Standish, 1991; Yu, et al., 1996; Zhang, et al., 1996), the tortuosity variation in this range of d/D is far from being known.

POROUS MEDIA MODELING

Although a simplified case of the tortuosity interpretation like geometrical ratio of channel length, λ , to porous medium thickness, L , will be considered below, $T = \lambda/L$, some properties of this parameter need to be discussed.

i) Modeling Parameters Estimation

Pore Geometry Analysis and Its Influence on Tortuosity: Different effects on tortuosity related with pore length and pore configuration may be considered.

PORE LENGTH (LENGTH TORTUOSITY): 1). Length tortuosity of straight pores - it is the most simple case. Tortuosity is understood as the ratio of pore length to porous media thickness. In capillary models, it means that pore diameter is constant and the pore is straight. Its main feature is the equidistance of flow streamlines. 2). Length tortuosity of curved pores - this case differs from the previous one by the curvature of the pore channel.

Under hydraulic or mass transfer points of view, these cases correspond to an increase in the length of the flow streamline or in the path of molecules in porous media.

THE TORTUOSITY OF BENT PORES WITH LARGE CURVATURE: Usually for these types of pores the condition of constant diameter or constant cross-section is not valid. The limit case is the zigzag pore. The flow streamlines are not equidistant. With large curvature two effects occur: inertial effect and constriction effect for macromolecules. Pore hydraulic resistance and effective diffusion are not depending on pore length only. Exactly the same path length may lead to quite different tortuosity. In this case, the traditional tortuosity definition $T = \lambda/L$, is no longer valid. Tortuosity becomes more complicated and an additional characteristic such as the number of bends or the fractal dimension is needed. Furthermore, we may consider that the observed constriction effect of macromolecule diffusion for small ratio (molecule size) / (pore size) can also be caused by the pore curvature.

PORE CONFIGURATION: 1). Symmetrical straight pore with variable cross-section area. Although the pore

may have a length equal to porous medium thickness, the average path of molecule or stream is not equal to the medium thickness. Only the trajectory that coincides with pore axis has a length equal to the medium thickness. In this case pores can be characterized by the ratio of largest to smallest diameters or cross-section area, or by means of stream trajectories. For this type of pores, several effects can be expected: inertia, constriction effects related with curvature of trajectories and constriction effects related with changing of pore cross-section.

2). Symmetrical bent pore with variable cross section. Pore length-bending increases the first two effects described in the previous case. 3). Gofer pores. In this case, to the above-mentioned effects, a new effect characterized by the amplitude and frequency of gofers is added. A regular gofer pore type is obtained if the frequency of wall bends in pore configuration increases. 4). Random pore channel is the most complicated type of pore, with random variation of both channel thickness and channel length between consecutive bends.

For a better understanding of the tortuosity impact on mass transfer and separation processes in mixed beds it is necessary to begin the investigation with simplified porous media models. As packed beds with spherical particles are more predictable from the point of view of porous media parameters, they will therefore be used in this work. The tortuosity will be considered from a geometrical point of view. Some types of binary and ternary mixed beds will be modeled to investigate the relationship of T with porous medium structure.

ii) Ratio of Particle Diameters in Mixtures

With the purpose of establishing the range of particle diameters ratio suitable for modeling binary and ternary mixtures let us consider the effect of particle diameters ratio and volume fraction of largest particle in the mixture on equivalent particle diameter d_s , which is usually used in equation (3) for permeability. Since in numerical modeling dimensionless values of particle diameter are more suitable they will be used below and equivalent particle diameter will be estimated as a function of particle diameters ratio in mixtures.

In mixed beds there are particles with diameters $d_1, d_2, \dots, d_i, \dots, d_n$ with corresponding volume fraction in the mixture $x_1, x_2, \dots, x_i, \dots, x_n$, and the equivalent particle diameter is as follows:

$$\frac{1}{d_s} = \sum_{i=1}^n \frac{x_i}{d_i} \quad (8)$$

In the particular case of a binary mixture:

$$\frac{1}{d_s} = \frac{x_D}{D} + \frac{(1-x_D)}{d} = \frac{1}{D} \left[\frac{D}{d} - \left(\frac{D}{d} - 1 \right) x_D \right] \quad (9)$$

where D is large particle diameter and d is small particle diameter.

The range of modeling particle diameter ratio was chosen as $n = D/d = 2-15$ (binary mixtures) and $n = D/d = 2-10$ (ternary

mixtures). These ranges cover the variation of T from 0.1 up to 1.

iii) Modeling of Packed Beds

For estimating the porosity, tortuosity and ratio variation in binary and ternary mixtures with different volume fractions of large particles, the following simulation procedure was used.

A two-dimensional model of the binary mixture was built by a method similar to the described by Suzuki et al. (1981) and Tory et al. (1973) with a difference in the final stage.

Series of particles (discs) of defined size ratio and numbers were used. For instance, for n large and m small discs, then $N = n + m$ where n and m are integer. The chamber was divided in several dropping channels. The channel through which each disc was dropped was randomly chosen. The width of the chamber was 750 pixels. Each falling particle either comes to rest on the bottom of the chamber or else will come into contact with one of the particles, which is already packed in the bed. After contact the disc rolls on the border of the disc which is already packed until contact is established with another disc. Then the disc is manually moved to the final position in order to provide the densest packing. The procedure is finished when a number of 1000 particles is attained. Finally image analysis was done to calculate the volume fraction of large particles in the mixture and void fraction.

The ternary mixture model is built by filling the void space of binary mixture with smaller discs. Solid deposition in porous medium during filtration or precipitation of solids from solution are real cases corresponding to the case of a binary mixture filled by small particles. Typical examples of two-dimensional charts of a binary and ternary are shown in Figure 1. We assumed ϵ_0 , T_0 , and, hence, η_0 , are independent of the particle diameter in a monosized bed.

The tortuosity measurement was done by means of image treatment. Trajectory of a test point was built on the basis of the following assumptions: the test point can move downward, only; in branching points the test point moves to the branch chosen on the basis of a minimal trajectory length. Tortuosity was calculated as the ratio of the estimated trajectory length of the test point to the height of the layer, that is

$$T = \frac{\sum_{i=1}^N \sqrt{(x_i - x_{i-1})^2 + (y_i - y_{i-1})^2}}{\sum_{i=1}^N (y_i - y_{i-1})} \quad (10)$$

where x_i , and y_i , are projections of straight bends on axis x and y , respectively, and N - is total number of segments in bending line. The mean value of the tortuosity was determined for 6 trajectories on every image.

Modeling results for three types of binary beds - particle size ratio in mixture $n = D/d = 21/11 = 1.91$, $D/d = 31/8 = 3.875$ and $D/d = 63/4 = 15.75$ as well as for ternary mixtures are presented below. The data may be consider as a boundary estimation of normalized ϵ/ϵ_0 , T/T_0 ,

and η/η_0 . Diameters used in the model are dimensionless. All data were normalized for monosized beds.

DISCUSSION

iv) Porosity

The variation of normalized porosity for a binary mixture with x_D , Figure 2a, is in agreement with dependence described by Abe and Hirose (1982) but the minimal porosity occurs for region of $x_D > 0.85$. This deviation increases when particle size ratio D/d is increased. On the other hand, the model shows the possibility of creating denser packings than the predicted by equations 6 and 7.

Modeling results of ternary mixtures created by filling the void space of the aforementioned binary mixtures with small particles of dimensionless diameter 2.7, are shown in Figure 2a. Points marked with left arrows belong to binary mixtures created by filling monosized beds of particles $D = 11$ and $D = 8$, respectively. Points marked with arrows (a) and (b) on Figure 2a, belong to binary mixtures created by filling monosized beds of particles $D = 31$ and $D = 21$ by particles with $d = 2.7$, respectively.

Data scattering found in ternary mixtures is probably related with small ratio of largest and smallest particle diameter to the diameter of intermediate fraction when the scale of the void space is considered for the intermediate particle as a discrete function. It will be necessary to take into consideration not only the ratio of largest and smallest particle diameter but also its ratio to the intermediate fraction size.

The finest volume fraction, which is possible to place in the void space of the binary mixture, is in all tests between 6 – 11%. So, we will not discuss the dependence of variables on volume fraction of fine particles. The region of minimal porosity for a ternary mixture is broader than in binary mixtures and a denser packing is obtained.

According to the theoretical model of Yu and Standish (1991) the maximal packing density for a ternary mixture with particle size ratio 31:8:2.7 must be around $\phi = 0.5$ and occurs when $\phi = 0.5375$ and the volume fraction of fine particles is 0.2875. A lower value for ϕ may be obtained by filling the binary mixture void spaces with fine particles.

v) Tortuosity

The tortuosity, as expected, depends on x_D and increased when the porosity decreased, but the x_D value for tortuosity maximum does not coincide with the x_D for the porosity minimum, Figure 2b. It means that the tortuosity is not only a function of the porosity but also a function of pore topology. As was mentioned above, there is a complicated relationship of tortuosity with porosity and packed bed structure.

The region of maximal tortuosity may be related to a qualitative change of pore size distribution in the mixture. Analysis of the frequency distribution of different pore fractions in a binary mixture shows that there is a transition zone from bimodal to unimodal distribution of pore size. The

maximum tortuosity location in our model correlates well with the above mentioned transition zone.

In ternary mixtures the tortuosity monotonously grows with increasing x_D and reaches the highest values when volume fraction of intermediate particles approaches zero, Figure 2b. Points marked with arrows belong to binary mixtures created by filling monosized beds of particles with $D = 21$ and $D = 31$ when the volume fraction of the intermediate particles equals zero. Scattering of the tortuosity data has the same nature of the ternary mixture porosity. Nevertheless it must be noted that the tortuosity of filled monosized beds, $n = 11.4$ and $n = 7.78$, is higher than for the binary mixture with 15.75.

It is important to find a lower bound for the tortuosity when minimal pathway is approached. In the case of a large value of D/d , $D/d > 10 - 15$, the tortuosity of a mixed binary bed in the range of maximal tortuosity may be interpreted as a complex value of two components. The range of maximal tortuosity may be characterized as a skeleton of large particles with void space completely filled by small ones.

The first component of the total tortuosity T represents a tortuosity, generated in the bed space by the large particles skeleton, T_D , named a macro-tortuosity. The second component of T represents the tortuosity of small particles fraction, filling void space of the skeleton, T_d , micro-tortuosity. According to this we have a pore structure shown in Figure 2b. The total pore length is equal to L_e (see the scheme, Figure 2b). The length of the line that corresponds to macro-tortuous path scale is L_D (see the scheme (c) on Figure 2b). Hence,

$$T_D = L_e / L_D \quad (11)$$

$$T_d = L_D / L \quad (12)$$

where L is the bed thickness.

The total tortuosity T , according to equation (11) and (12) can be written as

$$T = \frac{L_e}{L} = \frac{L_D T_D}{L} = T_D T_d \quad (13)$$

Since in both cases the tortuosity (T_D and T_d) is generated in a bed of spherical particles, we can assume for large values of D/d , in the range of maximal tortuosity T , that $T_D \approx T_d = T_0$, where T_0 is the tortuosity of a monosized spherical particle bed. Hence, in the two-dimensional

$$\text{model } T_0 = 1.1547 \text{ and } T = T_0^2 \text{ or } \frac{T}{T_0} = T_0 = 1.1547,$$

which is in good agreement with maximal normalized tortuosity $T/T_0 = 1.12$, measured for $D/d = 15.75$, Figure 2b.

Because this estimation was done for the minimal pathway in the mixed bed, we can use it as a low bound of

tortuosity for a two-dimensional mixed bed of spherical particles when $D/d \rightarrow \infty$. This approach can be expanded to the ternary mixture representing the tortuosity scale generated by intermediate particle fraction as T_i :

$$T = T_D \cdot T_i \cdot T_d \quad (14)$$

If $T_0 = 1.1547$ then we have for $D/d \rightarrow \infty$ the total tortuosity $T = T_0^3$ or $T/T_0 = T_0^2 = 1.333$. This value is quite different from measured values (maximal normalized tortuosity of ternary mixture is about 1.19). The difference may be explained by the small ratio of largest and smallest particle diameter to the diameter of intermediate fraction, which is not larger than 4, when the scale of the void space is considered for the intermediate particle as a discrete function.

As seen in equation (3), the permeability and effective diffusivity, equation (5), are a function of the ratio $\eta = \epsilon/T$ suggesting the possibility of controlling packed beds mass transfer properties by changing x_D , Figure 3. The comparison between the observed variation of the porosity and tortuosity values show that, for this particular case of dense packing model, the porosity is more affected than the tortuosity. As a consequence of the larger variation on the porosity, the ratio $\eta = \epsilon/T$ has a behavior that is similar to the one observed for the dependence of the porosity on x_D . Nevertheless, the theoretical calculation shows that the role of tortuosity in three-dimensional model becomes significant for the ratio $T/T_0 > 1.2$.

It may be seen that an amount as small as 6-10% of the fine particles in the mixture can reduce η 2-4 times and even more, Figure 3. This proves the significant role of a small fraction of the smallest particles in packed beds in transport phenomena in porous media.

Finally, for binary packing it must be pointed out that two different packings may have the same values for porosity, tortuosity or η and different volume fractions. This means that a hysteresis loop on the dependence of tortuosity vs. porosity or η vs. porosity may be expected. This fact must be taken into consideration when binary packing data are represented in terms of T vs. ϵ .

CONCLUSION

Two-dimensional modeling of binary and ternary mixed particle beds allowed to set some bounds for porosity, tortuosity and the ratio $\eta = \epsilon/T$. Different volume fractions of large and small particles in the mixture as well as different ratio of particle size were investigated.

The porosity changes with variation of the volume fraction of large particles in the mixture. The dependence of the porosity vs. volume fraction of large particles x_D of binary packing passed through a minimum. For binary dense packing, the minimal porosity is located in the range of a more large value of x_D than the predicted by Abe and Hirose (1982). For ternary mixture, built by means of filling the binary mixture

void space with fine particles, the region of minimal porosity became diffuse.

The tortuosity function vs. volume fraction of large particles passed through a maximum, which does not correspond to the minimum value of the porosity. The tortuosity's maximum is related to the transition zone from the bimodal to the unimodal pore-size distribution. With increasing ratio D/d the transition zone between bi- and unimodal distributions moves towards the more large volume fraction of large particles.

For binary mixtures two different packing may have the same porosity, tortuosity or ratio $\eta = \epsilon/T$ and different volume fraction, which indicates the existence of a hysteresis loop on the dependence of tortuosity vs. porosity. This fact must be taken into consideration when binary packing data are represented in terms of T vs. ϵ .

The introduction of the third fraction of fine particles into the binary model led to a dramatic decrease in porosity. For a volume fraction of smaller particles as low as 0.06 - 0.1 in the total volume of particles the porosity was 20 - 30% of monosized porous media. This reduction is more significant with the increase in the intermediate particle size ratio to the fine (third fraction) particle size.

The analysis shows that the characterization of a mixed bed must take in account other properties beside particle size. Different beds with similar equivalent particle diameter can have quite different porosity or tortuosity.

The ratio ϵ/T , which is a part of the permeability and effective diffusivity, also passed through a minimum. Therefore, for example, by varying x_D the effective diffusivity in the medium may undergo a decrease of 70% for binary mixtures and of 85% for ternary mixtures. This effect can be more significant for the case of the permeability because of the dependence on $(\epsilon/T)^2$ and $\epsilon/(1-\epsilon)^2$ (equation 3).

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REFERENCES

- Abbasi, M.H., Evans, J.W. and Abramson, I.S., "Diffusion of Gases in Porous Solids: Monte Carlo Simulation in the Knudsen and Ordinary Diffusion Regimes," *AIChE Journal*, Vol. 29, 1983, pp. 617-624.
- Abe, E. and Hirose, H., "Porosity Estimation of Mixed Cake in Body Filtration," *J. Chem. Eng. Japan*, Vol. 15, 1982, pp. 490-493.

- Bear, J., *Dynamics of Fluids in Porous Media*, Elsevier, New York, 1972.
- Carta, G. and Bauer, J.S., "Analytic Solution for Chromatography With Nonuniform Sorbent Particles," *AIChE Journal*, 1990, Vol. 36, pp. 147-150.
- Dullien, F.A.L., "Single Phase Flow Through Porous Media and Pore Structure," *Chem. Eng. J.*, Vol. 10, No. 1, 1975, pp. 1-34.
- Gotoh, K., Chuba, T. and Suzuki, A., "Computer Simulation of Weight Distributions of Spherical-Particle Beds on the Bottom of a Container," *Int. Chem. Eng.*, Vol. 22, No. 1, 1982, pp. 107-115.
- Hulewicz, Z.Z., "Resistance to Flow Through a Granular Bed in the Laminar Regime. I. Derivation of a New Correlating Equation," *Int. Chem. Eng.*, Vol. 27, No. 3, 1987, pp. 566-573.
- Klusáček, K. and Schneider, P., "Effect of Size and Shape of Catalyst Microparticles on Pellet Pore Structure and Effectiveness," *Chem. Eng. Sci.*, Vol. 36, 1981, pp. 523-527.
- Kuramae, M., "Investigation of Unsaturated Liquid Flow in a Granular Bed Using a Cubic-Lattice Pore Model," *Int. Chem. Eng.*, Vol. 22, No. 4, 1982, pp. 666-673.
- Lin, C.Y. and Slattery, J.C., "Three-Dimensional, Randomized, Network Model for Two-Phase Flow Through Porous Media," *AIChE Journal*, Vol. 28, No. 2, 1982, pp. 311-324.
- MacDonald, M.J., Chu, C.F., Guilloit, P.P. and Ng, K.M., "A Generalized Blake-Kozeny Equation for Multisized Particles," *AIChE Journal*, Vol. 37, No. 10, 1991, pp. 1583-1588.
- Macé, O. and Wei, J., "Diffusion in Random Particle Models for Hydrodemetalation Catalysts," *Ind. Eng. Chem. Res.*, Vol. 30, No. 5, 1991, pp. 909-918.
- McCune, C.C., Fogler, H.S. and Kline, W.E., "An Experimental Technique for Obtaining Permeability-Porosity Relationships in Acidized Porous Media," *Ind. Eng. Chem. Fundam.*, Vol. 18, No. 2, 1979, pp. 188-191.
- Olague, N.E., Smith, D.M. and Ciftcioglu, M., "Knudsen Diffusion in Ordered Sphere Packings," *AIChE Journal*, Vol. 34, 1988, pp. 1907-1909.
- Ouchiyama, N. and Tanaka, T., "Porosity of Mass of Solid Particles Having a Range of Sizes," *Ind. Eng. Chem. Fundam.*, Vol. 20, No. 1, 1981, pp. 66-71.
- Ouchiyama, N. and Tanaka, T., "Porosity Estimation for Random Packings of Spherical Particles," *Ind. Eng. Chem. Fundam.*, Vol. 23, No. 4, 1984, pp. 490-493.
- Suzuki, M., *Adsorption Engineering*, Elsevier, 1990.
- Suzuki, M., Makino, K., Yamada, M., et al., "A Study on the Coordination Number in a System of Randomly Packing, Uniform-Sized Spherical Particles," *Int. Chem. Eng.*, Vol. 21, No. 3, 1981, pp. 482-488.
- Tassopoulos, M. and Rosner, D.E., "Microstructural Descriptors Characterizing Granular Deposits," *AIChE Journal*, Vol. 38, 1992, pp. 15-25.
- Tory, E.M., Church, B.H., Tam, M.K. and Ratner, M., "Simulated Random Packings of Equal Spheres," *Can. J. Chem. Eng.*, Vol. 51, 1973, p. 484.
- Tsuchiya, K. and Furumoto, A., "Tortuosity of Bubble Rise Path in a Liquid-Solid Fluidized Bed: Effect of Particle Shape," *AIChE Journal*, Vol. 41, 1995, pp. 1368-1374.
- Wang, C.-H. and Smith, J.M., "Tortuosity Factors for Diffusion in Catalyst Pellets," *AIChE Journal*, Vol. 29, 1983, pp. 132-136.
- Wright, T., Smith, D.M. and Stermer, D.L., "Knudsen Diffusion in Bidisperse Mixtures of Uniform Spheres," *Ind. Eng. Chem. Res.*, Vol. 26, 1987, pp. 1227-1232.
- Yu, A.B. and Standish, N., "Estimation of the Porosity of Particle Mixtures by a Linear-Mixture Packing Model," *Ind. Eng. Chem. Res.*, Vol. 30, No. 6, 1991, pp. 1372-1385.
- Yu, A.B., Zou, R.P. and Standish, N., "Modifying the Linear Packing Model for Predicting the Porosity of Nonspherical Particle Mixtures," *Ind. Eng. Chem. Res.*, Vol. 35, No. 10, 1996, pp. 3730-3741.
- Zhang Z.P., Yu, A.B. and Oakeshott, R.B.S., "Effect of Packing Method on the Randomness of Disc Packing," *J. Phys. A.: Math. Gen.*, Vol. 29, 1996, pp. 2671-2685.
- Zhang, T.C. and Bishop, P.L., "Evaluation of Tortuosity Factor and Effective Diffusivities in Biofilms," *Water Research*, Vol. 28, 1994, pp. 2279-2287.
- Zou, R.P. and Yu, A.B., "Evaluation of the Packing Characteristics of Mono-Sized Non-spherical Particles," *Powder Technology*, Vol. 88, 1996, pp. 71-79.

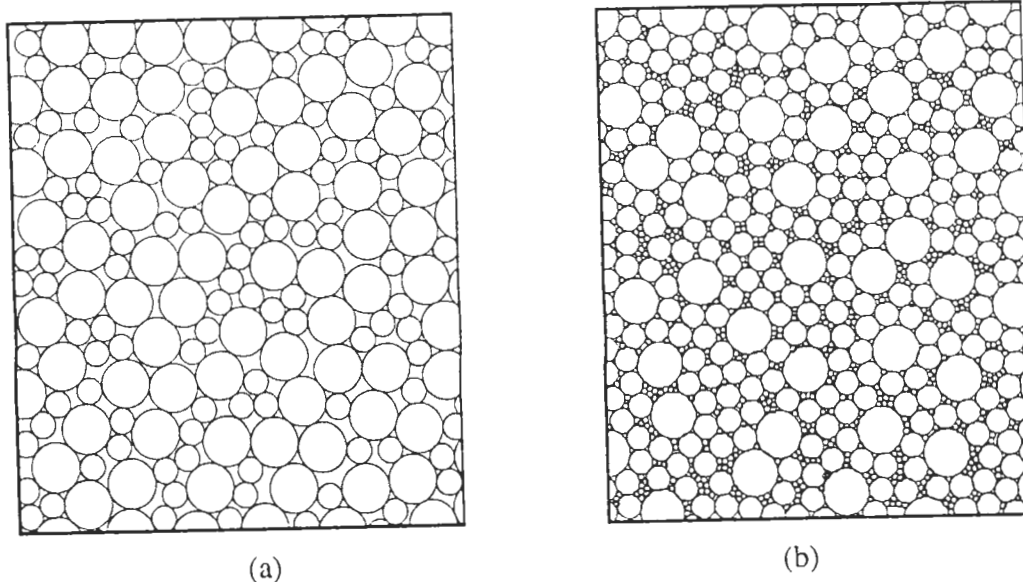


FIGURE 1. - Typical plots of porous media models for binary (a) and ternary (b) mixtures.
 (a), $n = 21/11 = 1.91$, $x_D = 0.727$, $\epsilon/\epsilon_0 = 0.776$, $T/T_0 = 1.088$ and $\eta/\eta_0 = 0.713$. (b), $m = 1.91$, $n = 7.78$, $x_D = x_1 = 0.3$, $x_2 = 0.11$, $x_3 = 0.5935$, $\epsilon/\epsilon_D = 0.314$, $T/T_0 = 1.04$ and $\eta/\eta_0 = 0.305$.

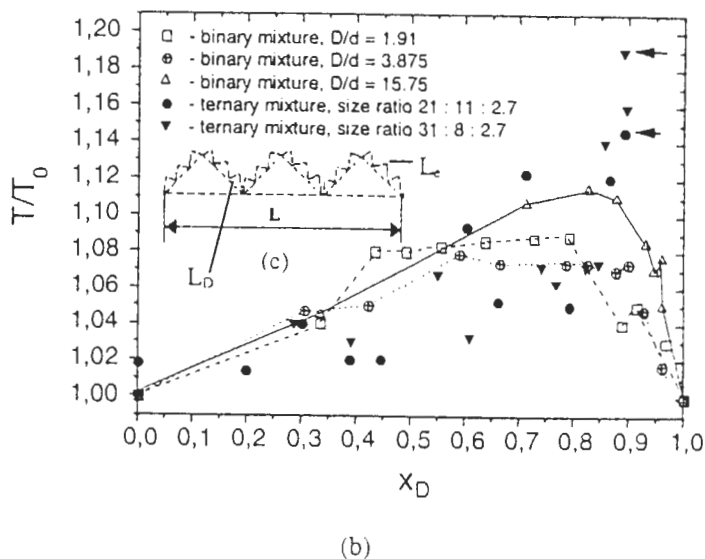
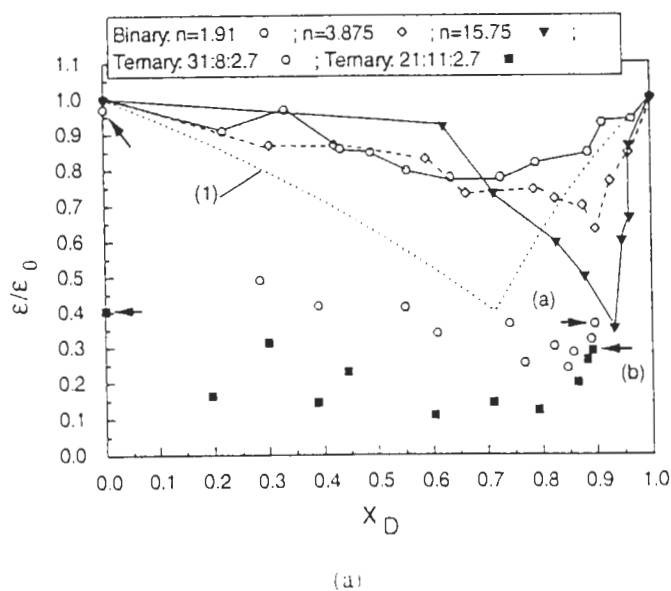


FIGURE 2. - Dependence of binary and ternary mixture the normalized porosity, ϵ/ϵ_0 , $\epsilon_0 = 0.407$, (a), and normalized tortuosity T/T_0 , (b), on x_D for different particle size ratio $n=D/d$ in the binary mixture and in ternary mixtures with size ratio 31:8:2.7, and 21:11:2.7. Curve (1) is prediction by equations 6 and 7 when $\epsilon_0 = \epsilon_d = \epsilon_D = 0.4$ and $d/D = 0$. (c), is a pore geometrical model in the range of maximal tortuosity. T_0 is the two-dimensional tortuosity of monosized particle layer, $T_0 = 1.1547$. Points marked with arrows belong to binary mixtures created by filling of the monosized beds with particles of diameter 2.7.

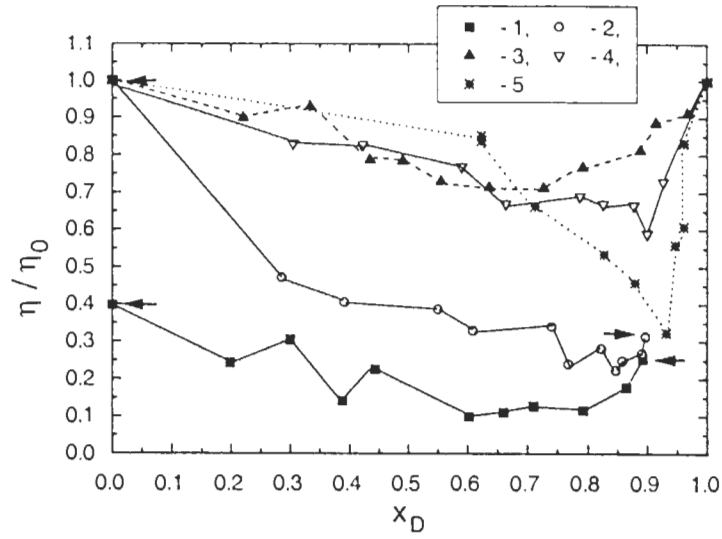


FIGURE 3. - Dependence of the binary and ternary mixture normalized value η/η_0 on volume fraction x_D for different particle size ratio. Here $\eta_0 = \epsilon_0/T_0$. 1 - ternary mixture, size ratio 21:11:2.7; 2 - ternary mixture 31:8:2.7; 3 - binary mixture, $n = 1.91$; 4 - $n = 3.785$; 5 - $n = 15.75$. Points marked with arrows correspond to binary mixtures when $d = 2.7$.