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Fractal scaling of effective diffusion coefficient of solute in porous media

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Abstract: Fractal approach is used to derive a power law relation between effective diffusion coefficient of solute in porous media and the geometry parameter characterizing the media. The results are consistent with the empirical equations analogous to Archie's law and are expected to be applied to prediction of effective diffusion coefficient.

Key words: diffusion; effective diffusion coefficient; fractal; porous media

Introduction

Diffusion may be the dominant mass transfer mechanism (compared to advection) in porous media of low permeability which are widely used as natural or artificial barriers for pollution control at waste disposal sites. Diffusion transport of contaminants through clay, silt, mudrock or shale formations as well as mineral liners and synthetic polymers has to be considered in site selection, risk assessment and engineering design of waste landfills (Johnson, 1988). Furthermore, the leaching of contaminants from solidified waste depends on molecular diffusion of the contaminants (Powell, 1992).

Modeling solute diffusion process in porous media requires information on diffusion coefficient which relates a flux to a driving force. Measurement of diffusion coefficient is time-consuming and highly variable, especially in porous media of low permeability, so prediction of this parameter is a viable alternative.

The classical approach to model diffusion in a porous medium is based on the hypothesis that the medium is invariant by translation, i.e. the medium looks the same at different locations and the randomness associated with it may be handled by a finite sample size or by statistical techniques. Modern fractal model, on the other hand, assumes that the medium is invariant by dilation, i.e. the medium looks identical under different magnifications. Natural porous media have been observed having hierarchical structure known as fractal scaling and characterized with a power law distribution between lower and upper limits of scale (Gimènez, 1997). Gimènez *et al*. (1997) have reviewed the derivations of classical semi-empirical power laws such as Archie's law and Campbell's law by assuming fractal scaling of various physical properties of a porous medium and the application of the laws to predicting soil-water retention and hydraulic conductivity. The objective of this paper is to derive a power law equation for predicting effective diffusion coefficient under steady state by using fractal approach.

1 Definition of effective diffusion coefficient

Solute diffusion in porous media is impeded by the tortuosity of the pores, the available cross sectional area (porosity) and possibly by the pore size distribution. Under steady state, the mass flux depends on the concentration gradient and is described by Fick's first law:

$$F = -D_e \frac{\mathrm{d}C}{\mathrm{d}x}. \tag{1}$$

Under water-saturated conditions C refers to the solute concentration in the pore water (ML^{-3}). D_e, the effective diffusion coefficient (L^2T^{-1}) is defined as:

$$D_e = \frac{D_{aq}\varepsilon}{\tau_f}, \tag{2}$$

D_{aq} is the diffusion coefficient in aqueous phase ($\mathrm{L^2T^{-1}}$). ε is the effective porosity of porous media which accounts for the reduced cross-sectional area available for diffusion when diffusion occurs only in the pore space. Since the natural porous medium always contains small pores which are not accessible for the solute and pores which do not contribute to the overall solute transport such as dead ends or blind pores, ε is smaller than the overall porosity (ϕ) of the porous medium (Lever, 1985). τ_f is tortuosity factor which accounts for the pore structure and is defined as the square of the ratio of the average pore length l_e (effective diffusion path) to

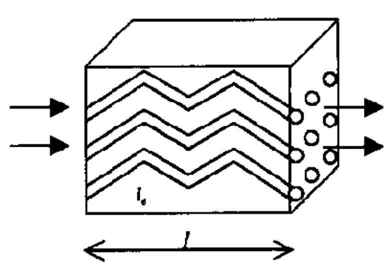

Fig.1 Sinuous capillary bundle model of porous media

the length of the porous medium l along the major flow or diffusion axis (Epstein, 1989):

$$\tau_f = \left(\frac{l_e}{l}\right)^2 = \tau^2, \tag{3}$$

τ is the tortuosity. Since in general $l_e > l$, $\tau > 1$. In fact, τ_f is a parameter of the one-dimensional capillaric model of the porous medium rather than a property of the medium (Grathwohl, 1997). The capillaric model (Fig.1) assumes the porous medium as a bundle of sinuous but parallel capillaries or pores.

2 Scaling of effective diffusion coefficient

In most cases, only the overall porosity (ϕ) of porous media can be obtained while both the effective porosity ε and the tortuosity factor τ_f are hardly to be determined. Analogous to Archie's law which is a widely-used empirical correlation describing the electrical conductivity in porous rocks, there has been an empirical power law formulation relating the effective diffusion coefficient D_e to the overall porosity ϕ of porous media:

$$D_e = D_{aq}\phi^m, \tag{4}$$

where m is an empirical exponent.

If the effective porosity ε is close to the overall porosity ϕ, i.e., $\varepsilon \approx \phi$, then:

$$D_e = D_{aq}\varepsilon^m, \tag{5}$$

the tortuosity factor τ_f can be connected with the effective porosity ε by combining Equations (2) and (5):

$$\tau_f = \varepsilon^{1-m}. \tag{6}$$

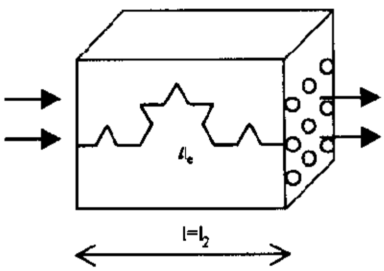

Fig.2 Fractal bundle model of porous media

Since Equations (5) and (6) are empirical and without solid physical and mathematical foundation, they have minimum impact on the understanding of diffusion phenomena in porous media, which limits their possibilities of extrapolating results to porous media outside the data set that was used to fit the equations.

Just like Archie' law, the power law form of Equations (5) and (6) is indicative of fractal geometry. In the sinuous capillary bundle model, the "sinuous" nature of the bundle reflects the roughness of pore-solid interface of the medium. Intensive studies (Gimènez, 1997) have suggested that pore-solid interface of porous media has fractal properties within some scale limits. Assuming that the bundle is so "sinuous" that it is a fractal (self-similar), e.g., Von Koch curve (Fig.2; Mandelbrot, 1982), the power law form of Equations (5) and (6) can be derived as follows.

Given a volume element of size l_2, a pore-solid interface fractal implies a simple relationship between the fractal dimension and the overall porosity of the medium (Katz, 1985):

$$\phi = \left(\frac{l_1}{l_2}\right)^{2-D_s}, \tag{7}$$

where D_s is the fractal dimension of pore-solid interface, and l_1 and l_2 are the lower and the upper limits of fractal region. For embedding dimension of two, $1 \leqslant D_s \leqslant 2$.

The tortuosity of the fractal bundle along which the solute diffuses in the volume element of size l_2 can be determined by:

$$\tau = \frac{l_e}{l} = \left(\frac{l_1}{l_2}\right)^{1-D_s}. \tag{8}$$

Substitution of Equations (7) and (8) into (2) gives

$$D_e = D_{aq}\left(\frac{l_1}{l_2}\right)^{D_s}. \tag{9}$$

Again $\varepsilon \approx \phi$ is assumed.

Equation (9) is equivalent to

$$D_e = D_{aq}\varepsilon^{\frac{D_s}{2-D_s}}; \tag{10}$$

$$\tau_f = \varepsilon^{\frac{2-2D_s}{2-D_s}}; \tag{11}$$

$$m = \frac{D_s}{2-D_s}. \tag{12}$$

Equations (10) and (11) are consistent with the empirical Equations (5) and (6), so a physical explanation of Equations (5) and (6) is given by the derivation of Equations (10) and (11). Equation (12) reveals that the empirical exponent m ($\geqslant 1$) is a parameter describing the roughness of the pore-solid interface of the porous medium. The rougher the interface, the larger the value of D_s, thus the larger the value of m.

According to Equations (11) and (12), $D_s = 1$ is equivalent to $m = 1$ and $\tau = 1$. As a result, Equation (10) retrieves to

$$D_e = D_{aq}\varepsilon, \tag{13}$$

which corresponds to the straight capillary bundle model of porous media.

In general, D_{aq} can be obtained from relevant literature, and $\varepsilon \approx \phi$ can be measured easily. D_s can be measured or determined by several specific techniques, such as scanning electron microscope images (Krohn, 1986), thin section photographs (Anderson, 1996), mercury porosimetry (Neimark, 1992), particle size distributions (Kravchenko, 1998) or water vapor adsorption (Sokolowska, 1999). Values of D_s for various porous media were reviewed by Gimènez *et al*. (1997), and the corresponding values of m can be calculated according to Equation (12). Some typical values of D_s and m are summarized in Table 1.

Table 1 Values of surface fractal, D_s, and calculated values of m for various porous media

Porous media	D_s	m	Reference
Clay	1.15—1.24	1.35—1.63	Anderson *et al*. (Anderson, 1996)
Clay	1.16—1.19	1.38—1.47	Anderson *et al*. (Anderson, 1996)
Clay loam	1.17—1.18	1.41—1.44	Anderson *et al*. (Anderson, 1996)
Clay loam	1.22—1.25	1.56—1.67	Gimènez *et al*. (Gimènez, 1997)
Silty clay loam	1.23	1.60	Anderson *et al*. (Anderson, 1996)
Silty loam	1.10 1.31	1.22 1.90	Young *et al*. (Young, 1991)

Table 1 shows that the values of m for all of the listed soils range from 1.22 to 1.90 with the average 1.51. The values above agree with $m = 3/2$, derived by Bruggemean (Grathwohl, 1997) under the assumption of isotropic packing of spherical particals; $m = 4/3$, reported by Millington and Quirk (Millington, 1960); $m = 1.5$, reported by Shimamura (Shimamura, 1992). Meanwhile, the values are comparable with Bear's (Bear, 1972) research on effective diffusion coefficient of unconsolidated sediments. Thus, Equations (10), (11) and (12) may be used to predict the effective diffusion coefficient of porous media.

3 Conclusion

A large amount of experimental evidence suggests that the morphology of porous media structure is fractal within some scale limits, therefore fractal geometry can be used to study the transport phenomena, e.g., diffusion in porous media. Under the assumption that the pore volume distribution and the pore-solid interface are fractals within a limited region, a power law equation is derived to show the relation between effective diffusion coefficient of solute in porous media and the geometry parameter characterizing the media. It is clarified that the empirical exponent m is a function of the pore-solid interact fractal dimension D_s. The derived equation is consistent with the empirical equation and gives the empirical equation a physical and mathematical explanation. Data collected from relevant literatures agree well with the equation. If the experimental data are available (under present research) with which to test the derived equation, the equation may be applied to the prediction of effective diffusion coefficient of solute in porous media.

References:

Anderson A N, 1996. Soil Sci Soc Am J [J], 60:962—969.
Bear J, 1972. Dynamics of fluids flow in porous media [M]. New York: Elsevier.
Epstein N, 1989. Chem Eng Sci [J], 44(3):777—779.
Gimènez D, Perfect E, Rawls W J *et al*., 1997. Soil Sci Soc Am J [J], 61:1285—1292.
Grathwohl P, 1997. Diffusion in natural porous media: contaminant transport, sorption/desorption and dissolution kinetics [M]. Boston: Klawer Academic Publishers.
Johnson R L, Cherry J R, Pankow J F, 1988. Environ Sci Technol [J], 23:340 - 349.
Katz A J, Thompson A H, 1985. Phys Rev Lett [J], 54:1325 - 1328.
Kravchenko A, Zhang R, 1998. Soil Science [J], 163(3):171 - 179.
Krohn C E, Thompson A H, 1986. Phys Rev B [J], 33(9):6366 - 6374.
Lever D A, Bradbury M H, Hemingway S J, 1985. J Hydrology [J], 80:45 - 76.
Mandelbrot B B, 1982. The fractal geometry of nature [M]. New York: W H Freeman.
Millington R J, Quirk J P, 1960. Transport in porous media [C]. In: 7th Intern. Congress of Soil Science, Madison, Wisc. 97—106.
Neimark A, 1992. Physica A [J], 191:258 - 262.
Powell M R, Mahalingam R, 1992. Environ Sci Technol [J], 26:507 - 511.
Shimamura K, 1992. Soil Sci [J], 153(4):274 - 249.
Sokolowska Z, Sokolowski S, 1999. Geoderma [J], 88:233 - 249.
Young I M, Crawford J W, 1991. Aust J Soil Res [J], 30:291 - 295.

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