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原著

다공성 미디아에 있어서 유효확산계수

김지형

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Effective Diffusion Coefficient in the Porous Media

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ABSTRACT

A diffusion process is often the main mechanism of soil gas/vapor movement in the vadose zone. The diffusion coefficients in the porous soil media are different from those in the free air phase by the reduction of available area for diffusion, tortuous diffusion path and variable cross section area along the diffusion path. To take account those effects of the diffusion process in the porous media, usually the terms of effective diffusion coefficient and tortuosity are have been used. However, as there are many differents definitions for the tortuosity, when the term of tortuosity is used, it is necessary to examine it throughly. Moreover, there are many different equations for the effective diffusion coefficient according to the investigators and the differences in the values of effective diffusion coefficients between the equations are not insignificant, the selection of the equation should be done with caution. In this paper, the different definitions of effective diffusion coefficient are examined and discussed. As well as definitions, the lots of availabe models for the diffusion coefficient in terms of porosities are compared. Also, the constrictiviy which explains the effect of cross sectional area change over the diffusion path was discussed.

Key words: diffusion, tortuosity, effective diffusion coefficient, constrictivity

요 약

토양내에서의 가스나 증기상의 오염물질의 이동은 여러 가지 현상에 의해서 일어나고 있으나 농도

차에 의해서 일어나는 확산이 가장 중요하다. 그런데 토양내에서의 확산은 토양 입자들로 인한 확산 부피의 감소, 또 확산 경로의 불규칙성, 확산 경로에 있어서 단면적의 변화 등으로 인해 대기중에서 일어나는 확산과는 다른 면을 보인다. 본 논문에서는 이러한 현상을 설명하기 위하여 흔히 사용되는 굴절계수(tortuosity), 유효확산계수(effective diffusion coefficient)의 서로 다른 그러나 같은 이름으로 사용되는 많은 정의들과 다양한 수학적 모델들에 대한 비교 검토가 이루어졌다. 굴절계수나 유효확산계수를 사용할 때는 각각의 경우 정의와 각 식의 특징에 대하여 세밀한 검토와 주의가 행하여져야 한다.

주제어: 확산, 굴절계수(tortuosity), 유효 확산 계수, 수렴계수(constrictivity)

Introduction

The transport of gas and vapor in the vadose zone of the soil media can occur by many different mechanisms such as density induced convective flow(Falta et al., 1989; Sleep and Sykes, 1989; Mendoza and Frind, 1990), thermal gradient(Marshall and Holmes, 1979), pressure gradient by barometric pumping(Turk, 1975; Freeze and Cherry, 1979) and diffusion by the concentration gradient. However, diffusion is the most important process in the soil media by which there is a net flux of molecules from regions of higher chemical potential or concentration into regions of lower chemical potential. This transport mechanism occurs in all forms or states of matter. In 1855, Adolph Fick introduced a theory, now known as Fick's first law of diffusion, which stated the diffusion of chemicals within various media was analogous to heat and electrical conduction as follows:

$$J = D\frac{\partial C}{\partial x} \qquad (1)$$

where J = diffusion flux ($M/L^2/T$), D = diffusion coefficient (L^2/T), C = chemical potential or concentration (M/L3), and x = distance (L).

The gas emissions models from the landfill or the land treatment facilities ususlly adopt this diffusion equation. However, the media in which the transport occurs are porous and the effect of porous media is considered into the equation. In this paper, the definitions and models of effective diffusion coefficient are examined and discussed. Also, the constrictiviy which explains the effect of cross sectional area change over the diffusion path is discussed

Porosity and tortuosity in the porous soil media

To describe the diffusive transport of gaseous pollutants through soil, Fick's law can be used. However within a soil matrix, not every cross sectional area is available for diffusion process, and diffusion occurs along irregular and tortuous paths. To illustrate this, Currie (1970) presented the diagram shown in Fig. 1 describing the effect of tortuosity and porosity on diffusion. Currie considered a volume element, or a block, of porous medium, of length and cross sectional area A in which there is a tortuous channel of length and cross sectional area A_e. Currie then related D/D_o to tortuosity as described below.

Fick's First Law, as applied to the tortuous channel of diagram 1) in Fig. 1, can be written as:

$$Q = -D_o \frac{A_e \Delta C}{L_e} \cdots\cdots (2)$$

where Q = diffusive mass flow (M/T), Ae = area perpendicular to the direction of the tortuous path of length L_e, ΔC = concentration difference, and D_o = diffusion coefficient for open gaseous transport.

For the block considered as a whole, the equation that corresponds to equation (1) above is:

$$Q = -D_o \frac{A \Delta C}{L_e} \cdots\cdots (3)$$

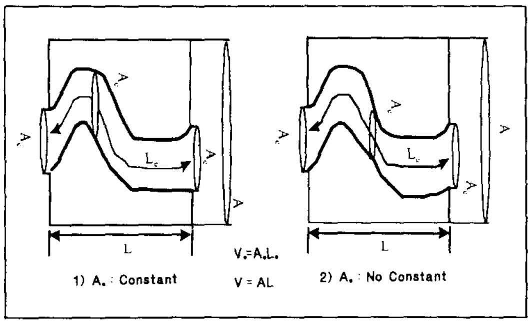

Fig. 1. Tortuosity model; diffusion length (Le) and area (Ae) as related to the block length and cross section.

Solving for D/D_o and considering the relationship of

$\varepsilon_a = \frac{V_e}{V} = \frac{A_e L_e}{AL}$ yields the following:

$$D = D_o \varepsilon_a \left(\frac{L}{L_e} \right)^2 \cdots\cdots (4)$$

and

$$Q = -D_o \varepsilon_a \left(\frac{L}{L_e} \right)^2 A \frac{\Delta C}{L} \cdots\cdots (5)$$

where = ε_a = air-filled porosity.

Here, tortuosity can be defined as:

$$\tau = \left(\frac{L}{L_e} \right)^2 \cdots\cdots (6)$$

The diffusion process through the soil matrix can then be expressed by the following equation for the description of mass transport along a tortuous path as flux with respect to the total cross-sectional area:

$$J = -D_o \varepsilon_a \tau \frac{\Delta C}{L} \cdots\cdots (7)$$

If the effective diffusion coefficient is defined by Eq. (8), which includes the effects of the tortuous diffusion path and reduction of cross-sectional area,

$$De = D_o \varepsilon_a \tau \cdots\cdots (8)$$

then the diffusive flux can be written as:

$$J = -D_e \frac{\partial C}{\partial x} = -D_e \frac{\Delta C}{L} \cdots\cdots (9)$$

However, different investigators have used various different definitions of tortuosity, as shown in Table 1. Also there are different corresponding definitions for the effective diffusion coefficient. Some include both tortuosity and air-filled porosity, and some exclude the air-filled porosity term. Therefore, values of tortuosity taken from the literature should be very carefully evaluated in order to be interpreted in a consistent manner.

Table 1. Various different definitions of tortuosity used in the literature

Definition	Reference
$\tau = \left(\frac{L_e}{L}\right)^2$	Carman(1937), Thibodeaux(1981), Thibodeaux(1982)
$\tau = \left(\frac{L_e}{L}\right)$	Collins(1976), van Brakel and Heettjes(1974)
$\tau = \left(\frac{L}{L_e}\right)$	Troeh et al. (1982)
$\tau = \left(\frac{L}{L_e}\right)^2$	Bear(1988)
$\tau' = \varepsilon_a \tau$	This equation includes the effects of tortuous path and reduction of area available for diffusion Herrera and Lang(1989) Gimmi et al. (1993)

Effective diffusion coefficient

Many investigators have sought to determine a general relationship between effective diffusion coefficient and the total porosity, air-filled porosity, or both for the diffusion of a gas in a porous medium. A sample of published relationships is presented in the Table 2, and predicted ratios of effective diffusion coefficient to the diffusion coefficient in air are shown in Fig. 2. As indicated in Fig. 2, a wide variation exists which results in part from the range in moisture contents used by the different investigators. Of the relationships listed in the Table 2, only those of Marshall (1959), and Millington (1959), Millington and Quirk (1961) are based on theoretical pore size distribution models and the rest are based on empirical relationships developed from laboratory data.

Table 2. Models of effective diffusion coefficient

Investigator	D_e / D_o	Remark
Buckingham (1904)	ε_a^2	soils
Bruggeman (1935)	$\varepsilon_a^{\frac{3}{2}}$	
Penman (1940)	$0.66\varepsilon_a$	soils,
Call (1957)	$0.66\left(\varepsilon_a - 1\right)$	
Millington (1959)	$\left(\frac{n}{m}\right)^2 \varepsilon_a^{\frac{4}{3}}$ (wet) $\varepsilon_a^{\frac{4}{3}}$ (dry)	m: number of equal parts n: drained number of equal parts
Marshall (1959)		theoretical (wet and dry)
Currie (1960)	$\gamma\varepsilon_a^{\mu}$	dry materials: =0.8-1, =1.4-11
Currie (1961)	$\gamma\varepsilon_t^{\mu-\sigma}\varepsilon_a^{\sigma}$	
Currie (1961)	$\frac{\varepsilon_a \frac{10}{3}}{\varepsilon_t^2}$	
Weissberg (1963)	$\frac{\varepsilon_a}{1+0.5(1-\varepsilon_a)}$	overlapping spheres possible
Grable (1968)	$10^{-6}\varepsilon_a^{3.36}$	
Currie (1970)	$\left(\frac{\varepsilon_a}{\varepsilon_t}\right)^4 \varepsilon_t^{\frac{3}{2}}$	
Lai (1976)	$\varepsilon_a^{\frac{5}{3}}$	

Among these, the expression of Millington and Quirk (1961) is the most frequently, almost exclusively, used equation in VOC emission models in the literature. Based on the Fick's first principles, Millington and Quirk (1961) derived the following relationship for the effective vapor diffusion coefficient:

$$\frac{D_e}{D_o} = \frac{\varepsilon_a^{\frac{10}{3}}}{\varepsilon_t^2} \qquad (10)$$

where ε_a = air-filled porosity and ε_t = total porosity.

However, equation (10) cannot be generally applicable to diffusion when pores of different sizes are present. Diffusive transport is proportional to the pore radius squared, and the distribution of pore sizes is needed in order to relate the effective vapor diffusion coefficient through the total porosity to the diffusion coefficient for open gaseous transport through the air filled porosity. Even so, this relationship has been shown to be very successful in soil media, and it is the most widely used form in the literature (Shear et al., 1966; Letey and Farmer, 1974; Farmer, 1978; Farmer et al., 1980; Jury et al., 1983). Jury et al. (1983) applied this expression to the pore water phase as well as pore space phase in the diffusion of pesticide in soil.

Currie (1960) performed hydrogen diffusion experiments with different types of dry porous media and suggested the following equation (11) for effective diffusion coefficient which includes the effects of internal geometry and porosity:

$$\frac{D_e}{D_o} = \gamma\varepsilon_a^{\mu} \cdots\cdots (11)$$

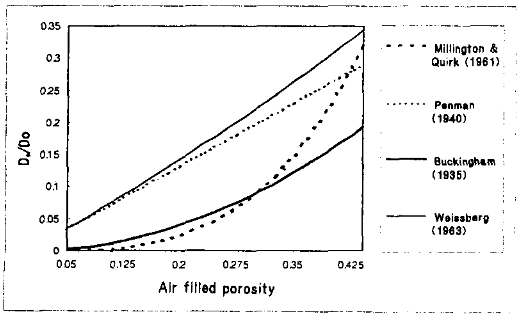

Fig. 2. Some examples of effective diffusion coefficient relationship in the Table 2.(total porosity = 0.45)

Where g, m = constants for a specific type of porous media. Moreover, Currie (1961) extended his study to examine the effect of moisture content which resulted in the following equation (Ehrenfeld et al., 1986):

$$\frac{D_e}{D_o} = \gamma\varepsilon_t^{\mu-\infty}\varepsilon_a^{\sigma} \cdots\cdots (12)$$

where = 4 for granular materials. The difficulty with equations such as (11) and (12) is that the appropriate values of parameters must be known in order to evaluate the effective diffusion coefficient. However, these parameters are different with different soil types, and not all the soil types are tested. Even though there are lots of different equations in terms of porosity for the effective diffusion coefficient, the equations of Millington and Quirk(1961) has been used widely.

However, as there are significant differences in the value of effective diffusion coefficients according to the equations, the appropriateness of the equation to the given soil condition should be examined before use. Also, the sensitivity analysis to the porosity should be examined, too. These analysis will be useful in the uncertainty analysis of the final model results.

Constrictivity

As shown in the diagram of 2) of Fig. 1, another variable in the transport of gas in the porous media is the cross sectional area change along the diffusion path. To consider that factor in the description of transport phenomena, the term of constrictivity is defined as follows:

$$\delta = \left(\frac{D_e}{\varepsilon_a D_o} \right) \quad \cdots\cdots (13)$$

where, δ = constrictivity.

The constrictivity accounts for the fact that the cross section of a segment varies over its length. The constrictivity can be measured by mercury porosimetry (van Brakel, 1974) but constrictivity has never been incorporated into the equations used to model VOC emissions. In fact, the effective diffusion coefficient really includes the variation of cross section change along the diffusion path in many empirical equations. Even using the theoretical equations for the effective diffusion coefficient in the transport model, they usually do not differentiate the effects between the tortuosity and constrictivity in the field data for the validation of that model. So, in the practical sense, the constrictivity is incorporated into the tortuosity or the effective diffusion coefficient.

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