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Modeling Species Transport by Concentrated Brine in Aggregated Porous Media

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Abstract. Basic equations governing the transport of species by concentrated brine flowing through an aggregated porous medium are developed. Some simple examples are solved numerically. The medium is considered to be composed of porous rock aggregates separated by 'macropores' through which the brine flows and transport of salt and low-concentration species takes place. The aggregates contain dead-end pores, cracks, and stationary pockets collectively called 'micropores'. The micropore space does not contribute to the flow, but it serves as a storage for salt and species. Adsorption of fluid species takes place at internal surface of aggregates where it is assumed that a linear equilibrium isotherm describes the process. The effects of high salt concentrations are accounted for in the brine density relation, the viscosity relation, Darcy's and Fick's laws, and the rate of mass transfer between macropores and micropores. Mass balance equations, supplemented by extended forms of Darcy's and Fick's laws, are employed to arrive at two sets of equations. One set consists of seven coupled equations for the salt mass fraction and fluid density in macropores, salt mass fraction in micropores, fluid velocity vector, and the fluid pressure. The other set consists of two coupled equations to be solved for the mass fractions of low-concentration species in micropores and macropores. Based on these equations, a mathematical model called TORISM is developed. Using this model, the potential significance of modifications to Darcy's Law are demonstrated.

Key words. Brine transport, species transport, radionuclides, aggregated porous media, micropores, macropores, structured porous media, Darcy's law, Fick's law.

1. Notation

a shape factor in Equation (30)
b shape factor in Equation (30)
$\mathrm{d}a$ infinitesimal element of area
D^f coefficient of density flow in the modified Darcy's law, $[L^2/T]$
$\mathbf{D}^i$ the diffusion-dispersion tensor for low-concentration species, $[L^2/T]$
$\mathbf{D}^s$ the diffusion-dispersion tensor for the salt component, $[L^2/T]$
D^{ia} macropore-micropore mass transfer rate coefficient for species, $[T^{-1}]$
$\mathbf{D}^{is}$ in the modified Fick's law, is the coefficient of low-concentration species transport due to the salt movement, $[L^2/T]$
D^{sa} macropore-microport mass transfer rate coefficient for salt, $[T^{-1}]$
D^i_m the coefficient of molecular diffusion of low-concentration species, $[L^2/T]$
D^s_m the coefficient of molecular diffusion of salt, $[L^2/T]$
$\mathbf{e}_g$ direction vector of the gravity

E^f rate of net exchange of mass between micropores and macropores, [M/L^3/T]
E^i rate of exchange of mass of low-concentration species between micropores and macropores, [M/L^3/T]
E^s rate of exchange of mass of salt between micropores and macropores, [M/L^3/T]
g magnitude of gravity vector, [L/T^2]
$\mathbf{g}$ gravity vector
G dimensionless constant defined in Equations (39)
j^s microscopic diffusive mass flux of salt, [M/L^2/T]
$\hat{j}^s$ effective microscopic diffusive mass flux of salt, [M/L^2/T]
J^{if} macroscopic diffusive-dispersive mass flux of low-concentration species, [M/L^2/T]
k permeability coefficient of the porous medium, [L^2]
K^{id} 'distribution coefficient' for adsorption of species on soil grains, [L^2/M]
l a resistance coefficient employed in Equation (26), [L]
L macroscopic characteristic length of the porous medium, [L]
n effective porosity of the porous medium (i.e., volume fraction of macropores)
n^{fp} normal unit vector at a micropore-macropore interface pointing into the micropore
p (micropore or macropore) fluid pressure [M/L/T^2]
p_0 a reference pressure
$\mathbf{q}$ Darcy velocity of macropore fluid, [L/T]
q_r reference flow velocity defined in Equations (39), [L/T]
r characteristic size of micropores, [L]
R characteristic size of macropores, [L]
R_f retardation factor defined in Equation (16)
S_0 specific surface of the porous medium, [L^{-1}]
S^i rate of adsorption of low-concentration species on soil grains, [M/L^3/T]
t time
t_0 time at which species are introduced at the lower boundary of the domain, [T]
t_1 time at which species mass fraction at the lower boundary of the domain is set to zero again, [T]
$t_{1/2}$ half-life of radioactive species, [T]
t_r reference time defined in Equation (39)
$\mathbf{v}$ microscopic velocity of the fluid, [L/T]
$\mathbf{v}^i$ microscopic velocity of the low-concentration component of the fluid, [L/T]
$\mathbf{v}^s$ microscopic velocity of the salt component of the fluid, [L/T]
$\mathbf{v}^f$ macroscopic mean velocity of the fluid, [L/T]

$\mathbf{v}^{if}$ macroscopic velocity of the low-concentration component of macropore fluid, [L/T]
$\mathbf{v}^{sf}$ macroscopic velocity of the salt component of macropore fluid, [L/T]
$\mathbf{w}$ (microscopic) velocity of the fluid-aggregate interface, [L/T]
X_1 defined in Equation (42a)
X_2 defined in Equation (42b)
Y_1 defined in Equation (42c)
Y_2 defined in Equation (42d)

Greek symbols

α^i dispersivity of low-concentration species, [L/T]
α^s dispersivity of salt, [L/T]
β coefficient of compressibility of brine, [LT²/M]
γ coefficient of dependence of brine density on salt mass fraction
δA^{af} total area of macropore-aggregate interfaces within an averaging volume
δA^{fg} total area of macropore-grain boundaries within an averaging volume
δA^{fp} total area of micropore-macropore interfaces within an averaging volume
δA^{pg} total area of micropore-grain interfaces within an averaging volume
δV volume of the averaging volume
ϵ total porosity of the porous medium
λ^i rate of decay of species, [T^{-1}]
μ dynamic viscosity of brine, [M/L/T]
μ_0 dynamic viscosity of fresh water, [M/L/T]
ρ microscopic mass density of the fluid, [M/L^3]
ρ_0 mass density of fresh water, [M/L^3]
ρ^i microscopic concentration of the low-concentration species, [M/L^3]
ρ^f microscopic mass density of the macropore fluid, [M/L^3]
ρ^p macroscopic mass density of the micropore fluid, [M/L^3]
ρ^s microscopic concentration of salt, [M/L^3]
ρ_0^g macroscopic mass density of soil grains, [M/L^2]
ρ^{if} macroscopic concentration of species in macropores, [M/L^3]
ρ^{ip} macroscopic concentration of species in micropores, [M/L^3]
ρ^{sf} macroscopic concentration of salt in macropores, [M/L^3]
ρ^{ip} macroscopic concentration of salt in micropores, [M/L^3]
ω^s microscopic mass fraction of salt, [M/M]
$\tilde{\omega}^s$ deviation of microscopic mass fraction of salt from its average value in the macropores, [M/M]
$\hat{\omega}^s$ difference between average mass fraction of salt in macropores and micropores, [M/M]
ω_0^i a reference mass fraction for low-concentration species, [M/M]
ω^{if} mass fraction of low-concentration species in macropores, [M/M]
ω^{ig} mass fraction of low-concentration species in soil grains, [M/M]

ω^{ip} mass fraction of low-concentration species in micropores, [M/M]
ω^{sf} mass fraction of salt in macropores, [M/M]
ω^{sp} mass fraction of salt in micropores, [M/M]

Superscripts
a aggregates
f macropore fluid
g soil grains
i low-concentration species
p (micro)pore fluid
s salt component

2. Introduction

In many countries, rock-salt formations are considered as a potential medium for the disposal of hazardous wastes and, in particular, high-level nuclear waste. The study of complicated physico-chemical processes involved in such situations is of the utmost importance in the safety assessment of disposal projects. An integral part of such studies is the proper description of the transport of pollutants released to the geosphere outside the host rock, e.g., after flooding of a waste repository placed in a salt formation. Often, a difficult problem of interest in this regard is the existence of (microscopic) pore structures in geological media which are in contact with rock-salt formations. Examples of such micro-structures are fractures and fissures in consolidated formations and secondary porosities in aggregated soils.

In recent years, many investigations have been directed towards study of the effect of microporosity on species transport (cf, Skopp and Warrick, 1974; van Genuchten and Wierenga, 1976, 1977; van Genuchten and Cleary, 1979; Rao *et al.*, 1980, 1982; Rasmusen, 1981; van Eijkeren and Loch, 1984; Crittenden *et al.*, 1986). In most of these studies, however, only one solute has been considered and that is assumed to exist at low concentrations such that it does not influence the density and motion of the fluid. But in the process of solute transport by brine in media around salt formations, two different species exist and one of them strongly affects the fluid density. The presence of high salt concentrations is also bound to influence the movement of low-concentration species. The effects of microporosity and salt presence are strongly coupled and their combined contribution is different from the simple addition of their individual effects. At present, little is known in this regard and much work needs to be done on studying the comgined effects of microporosity and high salt concentrations on the transport of species in structured media. The development presented here is a preliminary step in that direction.

In this work, a macroscopic description of the system is provided. Then, the basic equation describing the flow of brine and the transport of its components through macropores, and mass balance equations for brine and species in micropores are obtained. A resistance-type relation is developed to describe the exchange of mass between macropores and micropores. The effect of salt mass exchange between micropores and macropores on the species mass transfer into (or out of) aggregates naturally appears in this relation. The equations obtained here may be adopted for the case of fractured porous media as well. In the basic equations, adsorption and decay of species are also taken into consideration. Finally, using a one-dimensional model, species mass fraction profiles for a vertical column are calculated. By changing various parameters, the effect of salt concentration and macropore-micropore diffusion on species transport is illustrated. Note that in this work the word species is exclusively employed to indicate the low-concentration component of the brine.

3. Development of Basic Equations

Consider a porous medium in which soil grains have assembled closely together and in variety of configurations to form what we may call a "rock aggregate'. One may distinguish two types of pores in an aggregated porous medium: inter-aggregate pores or '*micropores*', and intra-aggregate pores or '*macropores*'. This distinction is subjective and is not necessarily based on a pore-size distribution. Micropores are considered to consist of dead-end pores, cracks, stationary pockets, and very tiny pores. Although these are connected to the overall pore space, by virtue of their geometry they contribute very little to the macroscopic transport of fluids through the medium. Therefore, they are also called "stagnant pores'. Nevertheless, micropores play an important role in the retardation of all species carried by the water.

Effectively, the macroscopic transport of water and its components takes place in macropores. Therefore, they are also called 'flowing pores'. Because of the large surface area of micropores compared to that of macropores, their role is particularly important whenever sorption and solution processes takes place.

Basically, there are two different approaches to the modelling of transport processes in aggregated porous media. One approach consists of solving the microscopic diffusion equation for one aggregate (of prescribed geometry) and then evaluating the total mass flux of species out of (or into) aggregates and using it as a source/sink term for the macroscopic dispersion equation which describes the transport in macropores (see, e.g., Rasmussen, 1981 or van Eijkeren and Loch, 1984). In the other approach, macroscopic mass balance equations are given for micropore as well as macropore species and the mass exchange between them is treated as a source/sink term for which an additional relation has to be provided (see, e.g., Rao *et al.*, 1980 and van Genuchten and Wierenga, 1976). We follow the second approach.

In a macroscopic view, one may assume that a saturated aggregated porous medium is filled with two different fluid phases: a stagnant phase (called *micropore* *fluid* or, simply, *pore fluid*) and a mobile or flowing phase (called *macropore fluid*). Similarly, fluid components and species extant to the micropore fluid and those in the macropore fluid, are considered as being different materials. Therefore, macroscopic equations of mass balance for multi-components multi-phase systems (cf. Bachmat and Bear, 1986; Hassanizadeh, 1986a) can be employed for micropore and macropore fluids (and their components) separately. To describe the motion of macropore fluid and its components, the extended versions of Darcy's and Fick's laws developed by Hassanizadeh (1986b) are employed.

In the development that follows, a number of implicit and/or explicit assumptions listed below, are imposed. These are either common assumptions of porous media flow theories or a consequence of the fact that the fluid species (other than salt) are assumed to exist at trace concentrations.

Assumption 1: The temperature of the system is constant.

Assumption 2: Soil grains of the rock matrix are incompressible and have a constant mass density ρ_0^g.

Assumption 3: In a macroscopic view, rock aggregates and their components (i.e. soil grains, micropore fluid and its salt component, and species extant to the aggregate) have zero macroscopic velocity. This means that they are not convected and that the **macroscopic** intra-aggregate diffusion is to be neglected. It must be evident that in this analysis, we work with the macroscopic values of mass density of micropore fluid and mass concentration of its components (i.e., values averaged over the pores of all aggregates within an averaging volume).

Assumption 4: Total porosity denoted by ϵ and effective porosity (i.e., the volume fraction of macropores) denoted by n, are constant. This is actually a consequence of Assumptions 2 and 3.

Assumption 5: At a given (macroscopic) point (i.e., within an averaging volume) the fluid in the micropores has the same thermodynamic pressure as the fluid in the macropores.

Assumption 6: There is only one species of interest and its decay products are not considered in the analysis.

Assumption 7: The species exist at such low concentrations that they do not affect the mass balance of macropore and/or micropore fluids.

Assumption 8: The process of adsorption/desorption of species takes place only within micropores and at the internal surface of rock aggregates.

Assumption 9: The rate of adsorption of species on internal surfaces of aggregates is much faster than the rate of their diffusion in the micropores. Therefore, one may assume that equilibrium exists between the solutes adsorbed on the surface of soil grains and the solute in the micropore fluid.

Some of these assumptions can be relaxed without much difficulty. For example, it would be rather straightforward to include more species and take into account production rates. Also, adsorption of species on surfaces of macropores can be readily accounted for. However, some other assumptions, such as those regarding temperature and porosity changes, whill require the introduction of additional equations and further complications of theory. In this study, in order to focus on the effects of salt concentration, the number of parameters are kept to a minimum.

3.1. EQUATIONS OF MASS BALANCE

The following equations are given in terms of average (or macroscopic) quantities. The exchange of mass between macropores and aggregates, and between micrpores and soil grains, is given in the form of a source/sink term.

Mass balance equations for the macropore fluid and its components

$$n\frac{\partial\rho^f}{\partial t} + \nabla\cdot(n\rho^f\mathbf{v}^f) = -E^f \tag{1}$$

$$n\frac{\partial\rho^{sf}}{\partial t} + \nabla\cdot(n\rho^{sf}\mathbf{v}^{sf}) = -E^s \tag{2}$$

$$n\frac{\partial\rho^{if}}{\partial t} + \nabla\cdot(n\rho^{if}\mathbf{v}^{if}) = -E^i - n\rho^{if}\lambda^i. \tag{3}$$

In these equations, superscripts f, s, and i stand for the macropore fluid, the salt, and the species, respectively. Also, superscripts sf and if stand for the salt and low-concentration components of the macropore fluid. The term E^f is the rate of net exchange of mass between the flowing fluid and aggregates within an averaging volume. It includes the effect of reverse diffusion of pure water out of micropores (into macropores) as well as the diffusion of salt into micropores. It is defined in terms of microscopic quantities through the following relation (Hassanizadeh, 1986a).

$$E^f = \frac{1}{\delta V}\int_{\delta A^{fp}} \rho(\mathbf{v}-\mathbf{w})\cdot\mathbf{n}^{fp}\,\mathrm{d}a, \tag{4}$$

where δV is the averaging volume, δA^{fp} designates the union of interfacial areas between micropores and macropores (i.e., exit areas of micropores) which lie wholly inside δV, ρ and $\mathbf{v}$ are microscopic mass density and velocity vector of the fluid, $\mathbf{w}$ is the velocity of macropore-aggregate interface, $\mathbf{n}^{fp}$ is the normal unit vector of the interface pointing into the micropores ($\mathbf{n}^{pf} = -\mathbf{n}^{fp}$), and $\mathrm{d}a$ is the infinitesimal element of area. Note that at low salt concentrations, where the fluid density changes very little, E^f may be neglected in comparison with other terms in Equation (1).

Similarly, E^s and E^i are the rate of transfer of mass of salt and species, respectively, between macropores and micropores. Their definitions in terms of microscopic properties are

$$E^s = \frac{1}{\delta V}\int_{\delta A^{fp}} \rho^s(\mathbf{v}^s - \mathbf{w})\cdot\mathbf{n}^{fp}\,\mathrm{d}a, \tag{5}$$

$$E^i = \frac{1}{\delta V}\int_{\delta A^{fp}} \rho^i(\mathbf{v}^i - \mathbf{w})\cdot\mathbf{n}^{fp}\,\mathrm{d}a. \tag{6}$$

Note that these exchange terms account for the transfer of mass from macropores into micropores and/or vice-versa.

Because one is always interested in the (dispersive) motion of fluid components and species with respect to that of the whole fluid, customarily Equation (2) is recast in terms of the salt mass fraction, ω^{sf}, and the dispersive mass flux, $\mathbf{J}^{sf}$, defined below.

$$\omega^{sf} = \rho^{sf}/\rho^f, \tag{7a}$$

$$\mathbf{J}^{sf} = n\rho^{sf}(\mathbf{v}^{sf} - \mathbf{v}^f) = n\rho^f\omega^{sf}(\mathbf{v}^{sf} - \mathbf{v}^f). \tag{7b}$$

Using Equations (1) and (7), Equation (2) becomes

$$n\rho^f\frac{\partial\omega^{sf}}{\partial t} + n\rho^f\mathbf{v}^f\cdot\nabla\omega^{sf} + \nabla\cdot\mathbf{J}^{sf} = -(E^s - \omega^{sf}E^f). \tag{8}$$

Employing definitions similar to (7) for the species mass fraction ω^{if}, and the dispersive mass flux $\mathbf{J}^{if}$, Equation (3) becomes

$$n\rho^f\frac{\partial\omega^{if}}{\partial t} + n\rho^f\mathbf{v}^f\cdot\nabla\omega^{if} + \nabla\cdot\mathbf{J}^{if} = -(E^i - \omega^{if}E^f) - n\rho^f\omega^{if}\lambda^i. \tag{9}$$

Note that λ^i is the rate of decay of species and has the dimension [M/M/T]. For radionuclide species, it would be equal to $\sqrt{2}/t_{1/2}$ where $t_{1/2}$ is the half-life of the radionuclide.

Mass balance equations for the micropore fluid and its components

Here, because of Assumption 3, the micropore fluid and its components are not convected nor dispersed. Therefore, equations similar to (1), (8), and (9), without convective and dispersive terms, will be obtained.

$$(\epsilon - n)\frac{\partial\rho^p}{\partial t} = E^f, \tag{10}$$

$$(\epsilon - n)\rho^p\frac{\partial\omega^{sp}}{\partial t} = E^s - \omega^{sp}E^f, \tag{11}$$

$$(\epsilon - n)\rho^p\frac{\partial\omega^{ip}}{\partial t} = (E^i - \omega^{ip}E^f) - (\epsilon - n)\rho^p\omega^{ip}\lambda^i - S^i, \tag{12}$$

where $(\epsilon - n)$ is equal to the volume fraction of micropores, ω^{sp} $(=\rho^{sp}/\rho^p)$ and ω^{ip} $(=\rho^{ip}/\rho^p)$ are mass fractions of the salt and species in the micropores, and S^i

is the rate of adsorption of species on the internal surfaces of aggregates. Note that the superscript p stands for the (micro)pore fluid.

Mass balance for species extant to soil grains

$$(1-\epsilon)\rho_0^g \frac{\partial \omega^{ig}}{\partial t} = S^i - (1-\epsilon)\rho_0^g \omega^{ig}\lambda^i, \tag{13}$$

where $(1-\epsilon)$ is the volume fraction of soil grains and ω^{ig} is the mass fraction of species extant to the soil grains. Acknowledging Assumption 7, it is proposed that any change in the mass fraction of species in micropores brings about an instantaneous change in the mass fraction of adsorbed species. Assuming a linear relationship, we may write:

$$\omega^{ig} = K^{id}(\omega^{sp})\rho^{ip} = K^{id}(\omega^{sp})\rho^p\omega^{ip}. \tag{14}$$

In this relation K^{id} is the 'distribution coefficient' which is generally a function of temperature, species concentration, salt mass fraction, pH, Eh, etc. Here, however, we have assumed that at constant temperature and constant pH, it is only a function of the mass fraction of salt in the micropores. Substitution of Equations (13) and (14) in (12) and division by ρ^p yields

$$(\epsilon - n)R_f \frac{\partial \omega^{ip}}{\partial t} = (E^i - \omega^{ip}E^f)/\rho^p - \Bigg[(\epsilon - n)R_f\lambda^i + (1-\epsilon)\rho_0^g\left(\frac{\mathrm{d}K^{id}}{\mathrm{d}\omega^{sp}} + \gamma K^{id}\right)\frac{\partial \omega^{sp}}{\partial t} + (1-\epsilon)\rho_0^g K^{id}\beta\frac{\partial p}{\partial t}\Bigg]\omega^{ip}, \tag{15}$$

where

$$R_f = 1 + (1-\epsilon)\rho_0^g K^{id}/(\epsilon - n). \tag{16}$$

At low-concentration situations, where ρ^p and K^{id} do not depend on salt concentration, R_f would be the same as the commonly employed 'retardation factor'. Note that terms involving K^{id} inside the parentheses in the right-hand side of Equation (15) will be absent in low-concentration situations.

3.2. EQUATIONS OF MOTION

All existing transport models employ Darcy's and Fick's laws to describe the motion of fluids and solutes, respectively. However, there is no experimental evidence to support the validity of these relations for situations where high salt concentrations and large concentrations gradients prevail. On the contrary, theoretical studies have indicated that the present form of these equations may need to be modified for high-concentration situations (see, e.g., Hassanizadeh, 1986b; Lever and Jackson, 1985, who consider Darcy's law; and de Marsily *et al.*, 1987, who consider Fick's law). Therefore, here the modified forms of those equations suggested by Hassanizadeh (1986b), applicable to high-concentration situations, are employed.

Extended Darcy's law

$$\mathbf{q} = -\frac{k}{\mu}(\nabla p - \rho^f g) - D^f \nabla \omega^{sf} \tag{17}$$

where $\mathbf{q} = n\mathbf{v}^f$ is the specific discharge (also known as Darcy's velocity) and D^f is the coefficient of density flow. The last term in equation (17) accounts for the net flux of mass of brine as a result of movement of salt under its own concentration gradient. At low salt concentrations, this term will be negligible (Hassanizadeh, 1986b). An intuitive argument to support the need for having an additional term in Darcy's equation can be given as follows. Salt may comprise up to 25% of concentrated brine. Thus, movement of the salt implies the movement of 25% of the fluid. We know that salt moves under its own concentration gradient. Therefore, the salt concentration gradient invokes a (direct) mass flux of the fluid. This is exactly what the additional term in Equation (17) stands for.

Extended Fick's law

A similar argument holds about the effect of salt movement on the transport of low-concentration species. As the salt moves, it carries other species along in the same way that the water component of brine does. This results in a mass flux of species in excess to their advective transport. Therefore, an additonal term in Fick's law employed for low-concentration species will be necessary to account for this effect.

$$\mathbf{J}^{sf} = -\rho^f \mathbf{D}^s \cdot \nabla \omega^{sf}, \tag{18a}$$

$$\mathbf{J}^{if} = -\rho^f \mathbf{D}^i \cdot \nabla \omega^{if} - \rho^f \omega^{if} \mathbf{D}^{is} \cdot \nabla \omega^{sf}, \tag{18b}$$

where $\mathbf{D}^s$ and $\mathbf{D}^i$ are the dispersion tensors for salt and species and $\mathbf{D}^{is}$ is the coefficient of species transport due to the salt movement. The latter term will be negligible at low salt concentrations (Hassanizadeh, 1986b). Dispersion tensors are assumed to be functions of velocity. Note that in comparison with equations suggested by Hassanizadeh (1986b), here we have neglected terms due to pressure diffusion.

3.3. EQUATIONS OF STATE

Equations of mass balance and motion have to be supplemented by relationships between thermodynamic pressure p, mass density ρ, salt mass fraction ω, and the temperature. Leaving the temperature out, the following equation for brine density is employed.

$$\rho^f = \rho_0 \, e^{\beta(p-p_0)+\gamma\omega^{sf}}, \tag{19}$$

where ρ_0 is the mass density of pure water at the reference pressure p_0 and at the reference temperature, and β and γ are assumed to be functions of temperature only. These values at 20°C and one atmosphere pressure are (*Handbook of Chemistry and Physics*, 1982):

$$\rho_0 = 998.23\ \mathrm{kg/m^3}, \qquad \beta = 4.5 \times 10^{-10}, \qquad \gamma = 0.6923. \tag{20}$$

The value of γ is obtained by fitting Equation (19) to data in the *Handbook of Chemistry and Physics*. A relation similar to (19) holds for ρ^p.

$$\rho^p = \rho_0\, \mathrm{e}^{\beta(p-p_0)+\gamma\omega^{sp}}. \tag{21}$$

Note that because of Assumption 5, the micropore fluid is assumed to have the same pressure as the macropore fluid. This serves as a restrictive condition on ρ^p. In other words, ρ^p may not be treated as an independent variable anymore. Therefore, the mass balance equation (10) may be regarded as a relation for the unknown quantity E^f.

Dependence of the dynamic viscosity on salt mass fraction at a constant temperature, can be described by a polynomial relation. The following relation is suggested by Lever and Jackson (1985) in an alternative form.

$$\mu = \mu_0(1 + 1.85\omega^s - 4.1\omega^{s^2} + 44.5\omega^{s^3}). \tag{22}$$

3.4. APPROXIMATE RELATIONS FOR E^s AND E^i

To close the set of equations developed in the previous sections, we need to provide constitutive relations for E^f, E^s, and E^i. However, as discussed above (below Equation (21)), Equation (10) already serves as a relation for E^f. Thus, one needs to develop relations only for E^s and E^i.

Consider definitions of E-terms given by Equations (4)–(6). Because it is assumed that the aggregates are not moving (Assumption 2) $\mathbf{w}$ may be identically set to zero.

Next, introducing the microscopic mass fraction $\omega^s(=\rho^s/\rho)$ and the microscopic diffusive flux $\mathbf{j}^s(=\rho^s(\mathbf{v}^s - \mathbf{v}))$, Equation (5) can be recast in the following form

$$E^s = \frac{1}{\delta V}\int_{\delta A^{fp}} \omega^s \rho \mathbf{v} \cdot \mathbf{n}^{fp}\, \mathrm{d}a + \frac{1}{\delta V}\int_{\delta A^{fp}} \mathbf{j}^s \cdot \mathbf{n}^{fp}\, \mathrm{d}a. \tag{23}$$

Now, set $\omega^s = \omega^{sf} + \tilde{\omega}^s$, where $\tilde{\omega}^s$ is the deviation of ω^s from average mass fraction of salt in the macropores. Within an averaging volume, ω^{sf} is constant and can be pulled out of the integral. Therefore, substituting relation (14) for E^f, Equation (23) becomes

$$E^s = \omega^{sf} E^f + \frac{1}{\delta V}\int_{\delta A^{fp}} \hat{\mathbf{j}}^s \cdot \mathbf{n}^{fp}\, \mathrm{d}a, \tag{24}$$

where $\hat{\mathbf{j}}^s = \rho\tilde{\omega}^s \mathbf{v} + \mathbf{j}^s$ is the effective diffusive mass flux of salt from macropores into micropores (or vice versa). As is customary, a Fickian-type relation is employed for $\hat{\mathbf{j}}^s$ so that (24) becomes

$$E^s = \omega^{sf}E^f - \frac{1}{\delta V}\int_{\delta A^{fp}} \mathbf{n}^{fp} \cdot (D^s_m \nabla \rho^s)\,\mathrm{d}a$$

$$= \omega^{sf}E^f - \frac{1}{\delta V} D^s_m \int_{\delta A^{fp}} \frac{\partial \rho^s}{\partial n}\,\mathrm{d}a, \tag{25}$$

where D^s_m is the molecular diffusion coefficient of salt, assumed to be constant within the averaging volume, and $\partial/\partial n$ denotes the derivative in the direction normal to the micropore-macropore interface (pointing into the micropores). The integral in this equation may be represented by a resistance-type relation in terms of average values of salt concentration in micropores and macropores

$$\int_{\delta A^{fp}} \frac{\partial \rho^s}{\partial n}\,\mathrm{d}a = \delta A^{fp}(\rho^{sp} - \rho^{sf})/l, \tag{26}$$

where l is a resistance length of the order of magnitude of aggregates radius. It is a microscopic characteristic length over which changes in microscopic salt concentration occur. This is an unknown of the theory which is later lumped with other coefficients. Eventually, such coefficients have to be determined experimentally. Now, Equation (25) becomes

$$E^s = \omega^{sf}E^f - \frac{\delta A^{fp}}{\delta V} D^s_m l^{-1}(\rho^{sp} - \rho^{sf}). \tag{27}$$

The ratio $\delta A^{fp}/\delta V$ depends on the total and effective porosities, specific surface of micropores, and the size and geometry of micropores and aggregates. The following relation is developed in the Appendix:

$$\frac{\delta A^{fp}}{\delta V} = S_0(\epsilon - n)\bigg/\left[a(1-n) + \left(\frac{bR}{r} - 1\right)(\epsilon - n)\right], \tag{28}$$

where S_0 is the specific surface of the medium, and r and R are the characteristic sizes of micropores and macropores, respectively. Coefficients a and b are shape factors and depend on the geometry of aggregates and micropores. For example, for spherical aggregates and cylindrical micropores, $a = 3$, $b = 2$; for spherical aggregates and conical micropores, $a = b = 1$; and for cylindrical aggregates (with height $2R$) and cylindrical micropores, $a = 3$, $b = 2$.

Finally, substitution of (28) in (27) yields:

$$E^s = \omega^{sf}E^f + (\epsilon - n)D^{sa}(\rho^{sf} - \rho^{sp}) = \omega^{sf}E^f + (\epsilon - n)D^{sa}(\rho^f\omega^{sf} - \rho^p\omega^{sp}), \tag{29}$$

where

$$D^{sa} = S_0 D^s_m\bigg/\left[l\left(a(1-n) + \left(\frac{bR}{r} - 1\right)(\epsilon - n)\right)\right] \tag{30}$$

is a mass transfer rate coefficient which has the dimension of $[\mathrm{T}^{-1}]$.

An analogous procedure for E^i leads to the following relation.

$$E^i = \omega^{if}E^f + (\epsilon - n)D^{ia}(\rho^{if} - \rho^{ip}), \tag{31}$$

where

$$D^{ia} = D^{sa}D^i_m/D^s_m \tag{32}$$

and D^i_m is the molecular diffusion coefficient of the species. Obviously, one needs to evaluate the mass transfer rate coefficients D^{sa} and D^{ia} for a given medium. Two approaches are possible: (a) determine D^{sa} and D^{ia} directly from experimental data by curve fitting, (b) determine S_0 and D^s_m (or D^i_m) and use engineering judgement to select typical values for r, R, a and b, and determine l by curve fitting. Further studies in this regard are needed.

Relations similar to (29) (or 31) have been suggested by some other authors (cf. Rao *et al.*, 1980; van Genuchten and Wierenga, 1976). Their relations, however, are given for low concentration situations and do not contain the important term E^f which accounts for the effect of high salt concentration on macropore-micropore diffusion. At low salt concentrations, where ρ^f and ρ^p hardly change, E^f is very small and terms such as $\omega^{if}E^f$ and $\omega^{sf}E^f$ will be negligible. Then, our formulations reduces to those previously obtained by others.

3.5. RESUMÉ OF BASIC EQUATIONS

When combined, relations obtained in the previous sections constitute 9 equations in terms of 9 unknowns, ρ^f, ω^{sf}, ω^{if}, ω^{sp}, ω^{ip}, p, and $\mathbf{q}$. They can be divided into two distinct sets of equations. The first set consists of seven coupled equations to be solved for ρ^f, ω^{sf}, ω^{sp}, p and $\mathbf{q}$. In dimensionless form, they read as follows.

$$(1-\acute{\gamma}\hat{\omega}^s)\frac{\partial \acute{\omega}^{sp}}{\partial \acute{t}} = \acute{D}^{sa}(\acute{\omega}^{sf}\,e^{\acute{\gamma}\hat{\omega}^s} - \acute{\omega}^{sp}) + \hat{\omega}^s\acute{\beta}\frac{\partial \acute{p}}{\partial \acute{t}}, \tag{33}$$

$$n\frac{\partial \acute{\omega}^{sf}}{\partial \acute{t}} + \acute{\mathbf{q}}\cdot\acute{\nabla}\acute{\omega}^{sf} = \frac{1}{\acute{\rho}^f}\acute{\nabla}\cdot(\acute{\rho}^f\acute{\mathbf{D}}^s\cdot\acute{\nabla}\acute{\omega}^{sf}) - (\epsilon - n)\acute{D}^{sa}(\acute{\omega}^{sf} - \acute{\omega}^{sp}\,e^{-\acute{\gamma}\hat{\omega}^s}), \tag{34}$$

$$\acute{\beta}(n + (\epsilon - n)\,e^{-\acute{\gamma}\hat{\omega}^s})\frac{\partial \acute{p}}{\partial \acute{t}} - \frac{1}{\acute{\rho}^f}\nabla\cdot\left(\frac{\acute{\rho}^f}{\acute{\mu}}(\acute{\nabla}\acute{p} - \acute{\rho}^f G\mathbf{e}_g) + \acute{\rho}^f\acute{D}^f\acute{\nabla}\acute{\omega}^{sf}\right)$$

$$= -n\acute{\gamma}\frac{\partial \acute{\omega}^{sf}}{\partial \acute{t}} - (\epsilon - n)\acute{\gamma}\,e^{-\acute{\gamma}\hat{\omega}^s}\frac{\partial \acute{\omega}^{sp}}{\partial \acute{t}}, \tag{35}$$

$$\acute{\rho}^f = e^{\acute{\gamma}\acute{\omega}^{sf} + \acute{\beta}(\acute{p}-1)}, \tag{36}$$

$$\mathbf{q}' = -\frac{1}{\mu'}\left(\nabla' p' - \rho'^f G\mathbf{e}_g\right) - D'^f \nabla' \omega'^{sf}, \tag{37}$$

where,

$$\hat{\omega}^s = \omega'^{sf} - \omega'^{sp}. \tag{38}$$

In these equations, primed characters are dimensionless variables defined below.

$$\begin{aligned}
&\rho' = \rho/\rho_0, \qquad \omega' = \omega/\omega_0^s, \qquad p' = p/p_0, \qquad \nabla' = L \times \nabla, \\
&\mu' = \mu/\mu_0, \qquad \mathbf{q}' = \mathbf{q}/q_r, \qquad t' = t/t_r, \qquad t_r = L/q_r, \\
&\beta' = \beta p_0, \qquad \gamma' = \gamma\omega_0^s, \qquad G = \rho_0 g L/p_0, \qquad D'^{sa} = D^{sa} t_r, \\
&\mathbf{D}'^s = \mathbf{D}^s/q_r L, \qquad D'^f = D^f \mu_0 \omega_0^s/k p_0, \qquad q_r = k p_0/\mu_0 L,
\end{aligned} \tag{39}$$

where ω_0^s is a reference value for the salt mass fraction (an appropriate choice is the salt mass fraction of inflow brine), L is the macroscopic characteristic length of the medium, g is the gravity and $\mathbf{e}_g$ is its unit direction vector.

The second set of equations consists of the following two equations in terms of ω^{ip} and ω^{if}.

$$R_f \frac{\partial \omega'^{ip}}{\partial t'} + X_1 \omega'^{ip} = X_2 \omega'^{if}, \tag{40}$$

$$n\frac{\partial \omega'^{if}}{\partial t'} + (\mathbf{q}' - \mathbf{D}'^{is} \cdot \nabla' \omega'^{sf}) \cdot \nabla' \omega'^{if} - \frac{1}{\rho'^f} \nabla' \cdot (\rho'^f \mathbf{D}'^i \cdot \nabla' \omega'^{if}) + Y_1 \omega'^{if} = Y_2 \omega'^{ip}, \tag{41}$$

where,

$$\begin{aligned}
X_1 = R_f \lambda'^i + D'^{ia} &+ \left[\frac{1-\epsilon}{\epsilon - n}\rho'^g_0\left(\frac{\mathrm{d}K'^{id}}{\mathrm{d}\omega'^{sp}} + \gamma K'^{id}\right) + \gamma'\right]\frac{\partial \omega'^{sp}}{\partial t} + \\
&+ \beta'\left[\frac{1-\epsilon}{\epsilon - n}\rho'^g_0 K'^{id} + 1\right]\frac{\partial p'}{\partial t'},
\end{aligned} \tag{42a}$$

$$X_2 = D'^{ia} \mathrm{e}^{\gamma' \hat{\omega}^s} + \left(\gamma \frac{\partial \omega'^{sp}}{\partial t'} + \beta' \frac{\partial p'}{\partial t'}\right), \tag{42b}$$

$$Y_1 = (\epsilon - n) D'^{ia} + n\lambda'^i - \frac{1}{\rho'^f}\nabla' \cdot (\rho'^f D'^{is} \cdot \nabla' \omega'^{sf}), \tag{42c}$$

$$Y_2 = (\epsilon - n) D'^{ia}\, \mathrm{e}^{-\gamma' \hat{\omega}^s}. \tag{42d}$$

In these equations, the following dimensionless variables are employed.

$$\acute{\omega}^{if} = \omega^{if}/\omega_0^i, \qquad \acute{\omega}^{ip} = \omega^{ip}/\omega_0^i, \qquad \acute{D}^{ia} = D^{ia}t_r, \qquad \acute{K}^{id} = \rho_0 K^{id},$$

$$\acute{\lambda}^i = \lambda^i t_r, \qquad \acute{\mathbf{D}}^i = \mathbf{D}^i/q_r L \acute{\rho}_0^g = \acute{\rho}_0^g/\rho_0, \qquad \acute{\mathbf{D}}^{is} = \mathbf{D}^{is}\omega_0^s/q_r L \acute{\rho}_0^g = \rho_0^g/\rho_0 \tag{43}$$

where ω_0^i is a reference value for species mass fraction (an appropriate choice is the mass fraction of species at the boundary). Note that the second set of equations is dependent on the first set. In other words, after solving Equations (33)–(37), computed values of ρ^f, ρ^p, ω^{sf}, ω^{sp}, p, and $\mathbf{q}$ should be substituted in Equations (40)–(41).

In the above equations, appropriate relations are needed for dispersion tensors $\mathbf{D}^s$ and $\mathbf{D}^i$. They may be given as functions of flow velocity. In the one-dimensional simulations reported in the next section, the following relation has been employed for $\mathbf{D}^s$.

$$\mathbf{D}^s = nD_m^s + \alpha^s|\mathbf{q}|, \tag{44}$$

where α^s is the longitudinal dispersivity of the medium. A similar relation is employed for $\mathbf{D}^i$.

To the knowledge of the author, the above sets of equations which include the combined effect of salt concentration and soil aggregation on the transport of species, are given here for the first time. Therefore, it is difficult to make a direct comparison between these and other works. However, it can be readily verified that in low-concentration situations, Equations (33) and (34) reduce to equations being employed by other authors. This is because in such situations we will have ω^{sf} & $\omega^{sp} \ll 1$, $\gamma\hat{\omega}^s \ll 1$, $\exp(\gamma\hat{\omega}^s)^f \simeq 1$, $\rho^f \simeq \rho^p$, and D^f and $\mathbf{D}^{is}$ terms are negligible.

4. Numerical Experiments

It seems almost impossible to find analytical solutions for the two sets of equations developed here. This is due to strong nonlinearities and cross-coupling terms present in these equations. Even for a one-dimensional flow problem, one needs to resort to numerical techniques.

A one-dimensional numerical model called TORISM has been set up for solving Equations (33)–(37) and (40)–(41). Using this model, Hassanizadeh (1987) has demonstrated the potential effects of high salt concentrations and soil aggregation on species transport. However, no quantitative indication was provided for the range over which such effects actually become significant. Here, we provide results of additional numerical experiments in this regard.

Calculations are made for a vertical column of length L filled with an aggregated porous medium. We assume that the column is connected at the

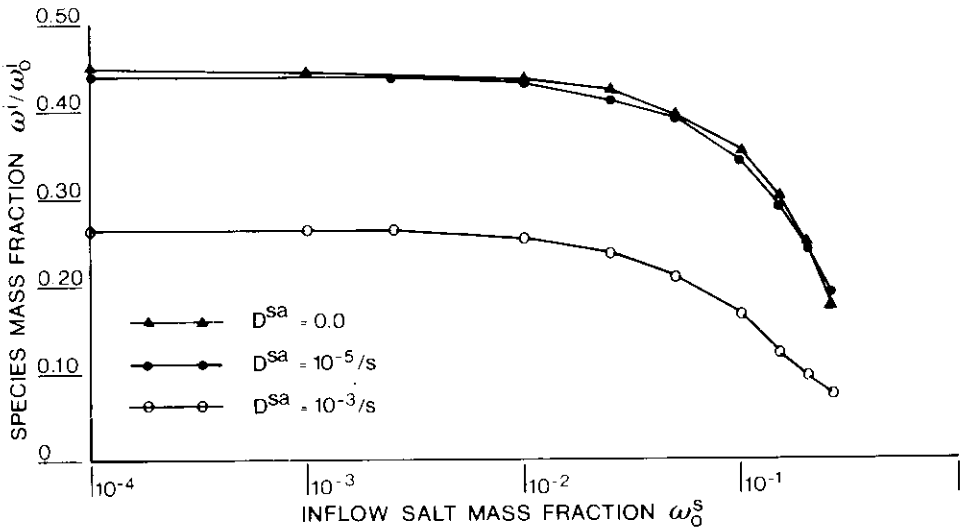

Fig. 1.

bottom to a reservoir of brine with constant mass fraction ω_0^s and constant pressure p_i, and at the top to a reservoir of fresh water at constant pressure p_0. The column is initially filled with fresh water, and then at time $t = 0$, the brine starts to flow in. Species at the constant mass fraction ω_0^i are introduced at the bottom of the column for a short period of time (from $t = t_0$ to $t = t_1$).

Both mass density and dynamic viscosity of brine increase with salt mass fraction. This causes the flow velocity to decrease, which in turn results in a slower movement of the species. This is illustrated in Figure 1 where the peak value of the mass fraction of species observed at the point $z = 0.25\ L$ is plotted as a function of the inflow salt mass fraction. The salt mass fraction of the inflow is actually a measure of concentration of brine that will eventually fill the column. It is evident that as the inflow salt concentration increases, species move slower and their peak value is reduced. Also, the macropore-micropore diffusion process has a pronounced effect. This is to be seen from Figure 1 where lower peak values are observed as higher values for mass transfer rate are employed. An interesting observation is that the effect of salt presence becomes pronounced only at salt mass fractions beyond 0.01 kg/kg (concentration ≈ 10 g/l). Below this value the salt component behaves as low-concentration species and its presence does not affect the movement of other species.

In addition to these direct effects, as explained in the previous section, one may need to modify Darcy's and Fick's laws at high salt concentrations, and introduce additional terms in these equations. Figures 2 and 3 give an indication of the significance of such additional terms. These figures illustrate that at low salt concentrations, the effect of D^f and D^{is} terms are actually negligible (upper

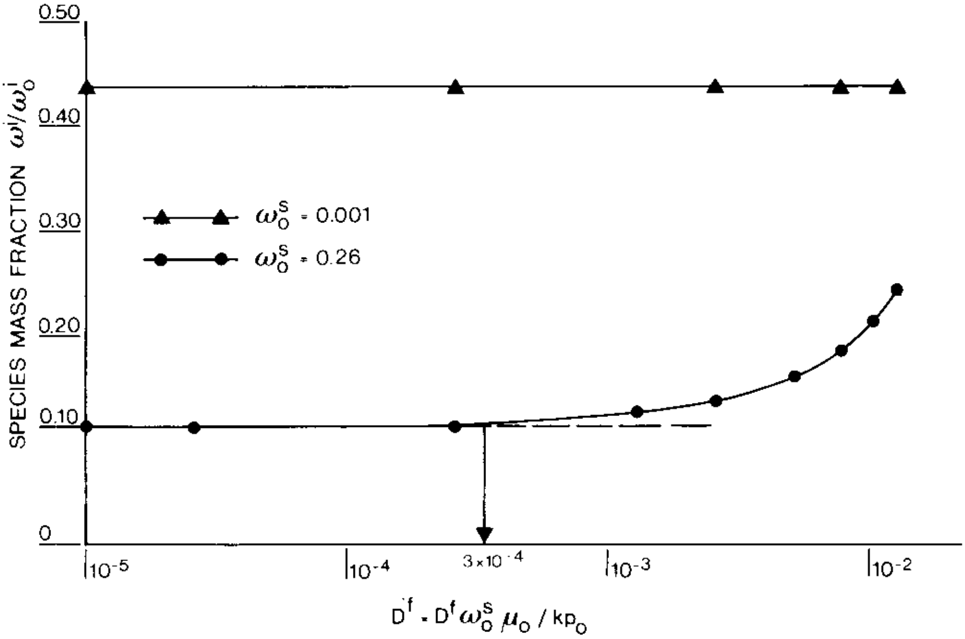
0.50
0.40
0.30
0.20
0.10
0
SPECIES MASS FRACTION ω^i/ω^i_o
ω^s_o = 0.001
ω^s_o = 0.26
10^{-5}
10^{-4}
3×10^{-4}
10^{-3}
10^{-2}
$\dot{D}^f = D^f \omega^s_o \mu_o / kp_o$

Fig. 2.

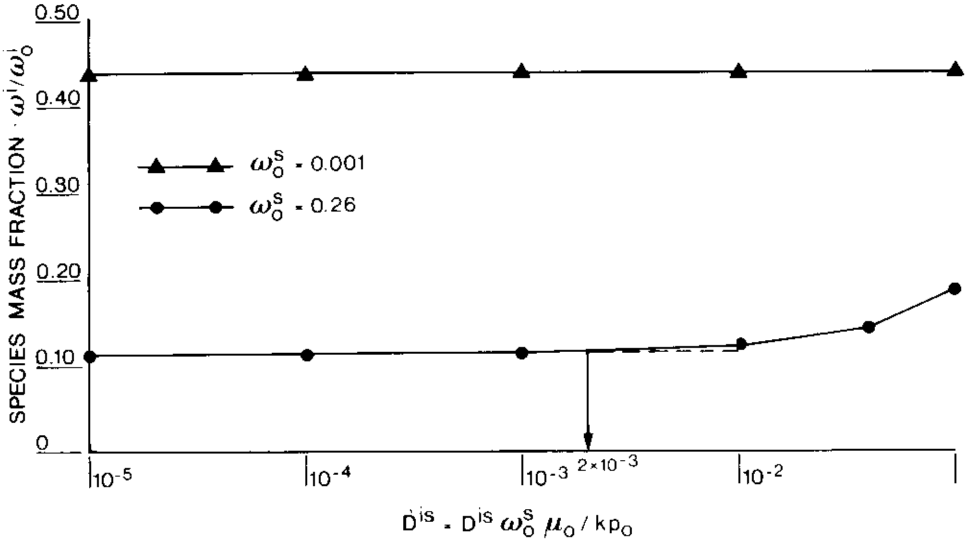
0.50
0.40
0.30
0.20
0.10
0
SPECIES MASS FRACTION ω^i/ω^i_o
ω^s_o = 0.001
ω^s_o = 0.26
10^{-5}
10^{-4}
10^{-3}
2×10^{-3}
10^{-2}
$\dot{D}^{is} = D^{is} \omega^s_o \mu_o / kp_o$

Fig. 3.

curves in Figures 2 and 3). Even at high salt concentrations, these terms become important only when they exceed certain critical values. From these figures, it may be estimated that these critical values are:

$$D^{f}_{\mathrm{crt}} = 3\times 10^{-4}\frac{kp_0}{\omega^s_0\mu_0} \quad \text{and} \quad D^{is}_{\mathrm{crt}} = 2\times 10^{-3}\frac{kp_0}{\omega^s_0\mu_0}.$$

Therefore, if in an actual situation the measured values of D^f and/or D^{is} for a given medium exceed these values, one must use modified Darcy's and Fick's laws presented in this work. Note that failing to take into account these additional terms, should they be important, will result in an underestimation of species mass transport which must be avoided in studies of hazardous waste disposal. In a recent article, Hassanizadeh and Leijnse [1988] have studied the effect of the additional terms in extended Darcy's law on the transport of salt itself, and, interestingly enough, the critical value obtained for D^f is exactly the same as that found here.

5. Conclusion

The two-phase approach has been successfully applied to the description of species transport by concentrated brine in an aggregated porous medium. In a macroscopic view, the medium can be considered to contain two different fluids: a stagnant fluid filling pores of aggregates (called pore fluid) and a moving fluid flowing through macropores (called macropore fluid). Similarly, fluid components resident in micropores and macropores can be considered as different entities. Appropriate equations for description of species transport by concentrated brine are developed. Based on the microscopic definition of micropore-macropore mass exchange terms, a resistance-type relation has been developed for them that takes into account the effect of high salt concentrations. A transfer rate coefficient which appears in this relation is given as a function of the characteristic sizes, porosity and shape of micropores and macropores, specific surface of the porous medium, and diffusion coefficient of the species.

The equations are numerically solved for a one-dimensional situation. It is shown that when the inflow salt mass fraction is less than 0.01 kg/kg, the salt component does not affect the movement of other species. However, beyond this value the movement of species is noticeably slowed down and they experience more dispersion as the inflow salt concentration increases. The effect of micropores largely depends on the value of the macropore-micropore mass transfer rate coefficient. Also the potential significance of modifications to Darcy's and Fick's laws are demonstrated. It is shown that beyond critical values

$$D^{f}_{\mathrm{crt}} = 3\times 10^{-4}\frac{kp_0}{\omega^s_0\mu_0} \quad \text{and} \quad D^{is}_{\mathrm{crt}} = 2\times 10^{-3}\frac{kp_0}{\omega^s_0\mu_0},$$

the effect of those modifications becomes pronounced.

6. Appendix A: A Relation for $\delta A^{fp}/\delta V$

Denote the specific surface area of the porous medium (i.e., surface of soil grains per unit volume of the medium) by $S_0 = (\delta A^{fg} + \delta A^{pg})/\delta V$ where δA^{fg} is the macropore-grain area and δA^{pg} is the micropore-grain area within the averaging volume. Therefore, $\delta V = (\delta A^{fg} + \delta A^{pg})/S_0$, and one can write

$$\frac{\delta A^{fp}}{\delta V} = S_0 \frac{\delta A^{fp}}{\delta A^{fg} + \delta A^{pg}} = S_0 \Big/ \left(\frac{\delta A^{fg}}{\delta A^{fp}} + \frac{\delta A^{pg}}{\delta A^{fp}}\right). \tag{A1}$$

But, also $\delta A^{fg} = \delta A^{af} - \delta A^{fp}$, where δA^{af} is the surface area of the aggregates (macropore-micropore area) within the averaging volume. Therefore,

$$\frac{\delta A^{fp}}{\delta V} = S_0 \Big/ \left(\frac{\delta A^{af}}{\delta A^{fp}} + \frac{\delta A^{pg}}{\delta A^{fp}} - 1\right). \tag{A2}$$

To evaluate these terms, let us denote the characteristic size of aggregates and micropores by R and r, respectively. Then, assuming that the length of micropores would be of the order of $R/2$ and denoting the total number of micropores within an aggregate by N, the following estimates can be made:

$$\delta A^{af} \propto R^2, \qquad \delta A^{fp} \propto Nr^2, \qquad \delta A^{pg} \propto NrR \tag{A3}$$

$$\delta V^a \propto R^3, \qquad \delta V^p \propto Nr^2 R, \tag{A4}$$

where δV^a and δV^p are the volumes of aggregates and micropores present within the averaging volume, and $\propto$ implies proportionality. From these relations, we obtain

$$\frac{\delta A^{af}}{\delta A^{fp}} = \propto \frac{R^2}{Nr^2} \propto \frac{\delta V^a}{\delta V^p} = \frac{1-n}{\epsilon - n}, \qquad \frac{\delta A^{pg}}{\delta A^{fp}} \propto \frac{R}{r}. \tag{A5}$$

As a result, Equation (A2) may now be written as

$$\frac{\delta A^{fp}}{\delta V} = S_0(\epsilon - n) \Big/ \left\{a(1-n) + \left(\frac{bR}{r} - 1\right)(\epsilon - n)\right\} \tag{A6}$$

where a and b are shape factors.

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