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Chemical Engineering Journal 80 (2000) 215–220

Chemical Engineering Journal

www.elsevier.com/locate/cej

Use of material coordinates in porous media solute and water flow

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Abstract

Material coordinates relating to water flow in saturated swelling systems and to solute movement during non-steady water flow in unsaturated porous materials often simplify descriptions of these processes. Furthermore, they may be formulated similarly and result in similar mathematical forms for the flow equations. The analysis may be extended to solute transport during non-steady flow of water in a deforming system. These space-like coordinates are simply defined and measured. Their use ensures material balance for all entities of concern and, for some important situations, results in a non-linear diffusion equation that may be solved for many practically important initial and boundary conditions. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Material coordinates; 1-Dimensional flow; Deforming systems; Solute flow

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1. Introduction

Material coordinates often simplify descriptions of water flow and solute transport in porous media. Thus, a coordinate based on the solid matrix may help analyze processes such as filtration and sedimentation because it removes the need to deal explicitly with the movement of water advected with the solid. The analysis then deals only with transfer of water relative to the matrix and a non-linear Fokker–Planck equation results where the water potential and the hydraulic conductivity are well-defined functions of the water content. This equation can often be simplified to a non-linear diffusion equation for which solutions are available for many practically important initial and boundary conditions [1–7].

Solute transfer during non-steady water flow in an unsaturated non-swelling porous media may be described similarly using a space-like coordinate based on the distribution and movement of the water. Transfer of solute is then described by a non-linear diffusion equation also [8,9].

Smiles et al. [10] examined a yet more complicated situation where the soluble salt, the clay and the water are all in motion making description of flow of any component in Eulerian space difficult. This situation is important in relation, for example, to the way retention pond liners react chemically and physically to effluents [11] and experiments such as those of [10] offer useful ways to examine these processes.

This paper shows that the derivation of material coordinates in each of these systems follows a similar argument, that the coordinate systems simplify material accounting and that the resulting equations form a common class for which solutions are available for many practically important initial and boundary conditions. It relies on more detailed argument presented in [12].

2. Formulation of flow equations

2.1. Water flow in swelling systems

During 1-dimensional, non-steady flow in a clay/water system the solid and liquid satisfy the material balance Eqs. (1) and (2):

$$\left(\frac{\partial \theta_{\mathrm{c}}}{\partial t}\right)_{z} = -\left(\frac{\partial F_{\mathrm{c}}}{\partial z}\right)_{t} \tag{1}$$

$$\left(\frac{\partial\,(\vartheta \theta_{\mathrm{c}})}{\partial t}\right)_{z} = -\left(\frac{\partial F_{\mathrm{w}}}{\partial z}\right)_{t} \tag{2}$$

where z and t are distance and time, respectively, θ_{c} and θ_{w} are volume fractions of solid and liquid, $\vartheta(=\theta_{\mathrm{w}}/\theta_{\mathrm{c}})$ is the moisture ratio and F_{c} (m s^{-1}) and F_{w} (m s^{-1}) are the volume fluxes of the solid and liquid. F_{w} is given by the equation:

$$F_{\mathrm{w}} = u + \vartheta F_{\mathrm{c}} \tag{3}$$

in which u (m s^{-1}) is the Darcy flux of water relative to the solid [13] and ϑF_{c} is the flux of water advected with the moving solid. Eqs. (1) and (3) give rise [14] to

$$\left(\frac{\partial \vartheta}{\partial t}\right)_{m} = -\left(\frac{\partial u}{\partial m}\right)_{t} \tag{4}$$

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PII: S1383-5866(00)00093-9

Nomenclature

C_s	solute concentration expressed per unit volume of solution, $\mathrm{mol_c\ m^{-3}}$
D_m (ϑ)	water diffusivity in material space, $\mathrm{m^2\ s^{-1}}$
D_s	effective diffusion coefficient of solute in porous material, $\mathrm{m^2\ s^{-1}}$
f	diffusive flux of solute relative to the water, $\mathrm{mol_c\ m^2\ s^{-1}}$
F_c	volume flux of solid in physical space, $\mathrm{m\ s^{-1}}$
F_s	flux of solute in physical space, $\mathrm{mol_c\ m^{-2}\ s^{-1}}$
F_w	volume flux of water in physical space, $\mathrm{m\ s^{-1}}$
j	material coordinate based on the distribution of the water, m
J	Boltzmann variable, $j/t^{1/2}$, $\mathrm{m\ s^{-1/2}}$
$k(\theta)$	hydraulic conductivity in physical space, $\mathrm{m\ s^{-1}}$
$k_m(\vartheta)$	hydraulic conductivity in material space, $\mathrm{m\ s^{-1}}$
m	material coordinate based on the solid distribution, m
M	Boltzmann variable, $m/t^{1/2}$, $\mathrm{m\ s^{-1/2}}$
p	material coordinate based on the distribution of water in m-space, m
P	Boltzmann variable, $p/t^{1/2}$, $\mathrm{m\ s^{-1/2}}$
S	sorptivity, $\mathrm{m\ s^{-1/2}}$
t	time, s
u	Darcy flux of water relative to the solid, $\mathrm{m\ s^{-1}}$
z	physical distance and gravitational potential of the water, m
Z	Boltzmann variable, $zt^{-1/2}$, $\mathrm{m\ s^{-1/2}}$

Greek letters

θ_w	volume fraction of water
θ_c	volume fraction of solid
Φ	total potential of the water, m
ψ	capillary potential (or effective stress), m
Ω	overburden potential, m
ϑ	moisture ratio

Subscripts

i	initial value
o	value at x=0

with $m(z, t)$ a material coordinate with dimensions of length [L] and units (m) defined by

$$\mathrm{d}m=\left(\frac{\partial m}{\partial z}\right)\mathrm{d}z+\left(\frac{\partial m}{\partial t}\right)\mathrm{d}t=\theta_\mathrm{c}\mathrm{d}z-F_\mathrm{c}\mathrm{d}t \tag{5}$$

m satisfies the material balance Eq. (1) for the solid and is evaluated by integrating Eq. (5) for appropriate conditions. Eq. (4) was explicitly stated by Terzaghi [12]; it arises, implicitly or explicitly in [2–4,6]. The formal definition of m in Eq. (5) is unusual: m appears generally to be defined, incompletely, in terms of the first term on the right-hand side of Eq. (5).

For 1-dimensional vertical flow in swelling systems, u is given by

$$u=-k\left(\theta_\mathrm{w}\right)\frac{\partial\Phi}{\partial z} \tag{6}$$

in which $k(\theta_\mathrm{w})$ is the water content dependent hydraulic conductivity (permeability divided by kinematic viscosity ($\mathrm{m^2\ s^{-1}}$)) and $\partial\Phi/\partial z$ is the space gradient of the total potential of the water, Φ.

$$\Phi=\psi+z+\Omega \tag{7}$$

with ψ the capillary potential (minus the effective stress), z the gravitational potential and Ω the overburden potential. If the potential components are defined per unit weight of water they take dimensions L and units m of water, so the hydraulic conductivity has dimensions LT^{-1} and units $\mathrm{m\ s^{-1}}$. We assume the effects of gravity to be relatively unimportant for illustrative purposes whence Darcy's law becomes

$$u=-k\left(\theta_\mathrm{w}\right)\frac{\partial\psi}{\partial z}=-k_m\left(\vartheta\right)\frac{\partial\psi}{\partial m}=-D_m\left(\vartheta\right)\frac{\partial\vartheta}{\partial m} \tag{8}$$

In Eq. (8), k_m (ϑ) is the hydraulic conductivity in m-space and D_m (ϑ) ($\mathrm{m^2\ s^{-1}}$) is the water diffusivity which may be defined only where $\psi(\vartheta)$ is single valued.

$$k_m\left(\vartheta\right)=\theta_\mathrm{c}k\left(\theta_\mathrm{w}\right)\quad\text{and}\quad D_m\left(\vartheta\right)=k_m\left(\vartheta\right)\frac{\mathrm{d}\psi}{\mathrm{d}\vartheta} \tag{9}$$

Substitution for u, using Eq. (8), in Eq. (4) results in

$$\left(\frac{\partial\vartheta}{\partial t}\right)_m=\frac{\partial}{\partial m}\left(D_m\left(\vartheta\right)\theta_\mathrm{c}\frac{\partial\vartheta}{\partial m}\right)_t \tag{10}$$

2.2. Non-reactive solute flow in non-swelling systems

Transfer of non-reactive solute during unsteady water flow in unsaturated non-swelling soil is approached in exactly the same way as the preceding example [8]. The material balance equations analogous to Eqs. (1) and (2) are

$$\left(\frac{\partial\theta_\mathrm{w}}{\partial t}\right)_z=-\left(\frac{\partial F_\mathrm{w}}{\partial z}\right)_t \tag{11}$$

$$\left(\frac{\partial\left(C_\mathrm{s}\theta_\mathrm{w}\right)}{\partial t}\right)_z=-\left(\frac{\partial F_\mathrm{s}}{\partial z}\right)_t \tag{12}$$

Eq. (11) is, in fact, identical with Eq. (2) but we present it in this way to preserve the analogy between systems one and two. In Eq. (12), F_s is the sum of the flux of solute with (f) and relative to ($C_\mathrm{s}\theta_\mathrm{w}$) the moving water ($\mathrm{mol_c\ m^{-2}\ s^{-1}}$), and C_s ($\mathrm{mol_c\ m^{-3}}$) is the solution concentration. That is (cf. Eq. (3))

$$F_\mathrm{s}=f+C_\mathrm{s}F_\mathrm{w} \tag{13}$$

and the analogues of Eq. (4) and Eq. (5) are

$$\left(\frac{\partial C_{\mathrm{s}}}{\partial t}\right)_{j} = -\left(\frac{\partial f}{\partial j}\right)_{t} \tag{14}$$

$$\mathrm{d}j = \left(\frac{\partial j}{\partial z}\right)\mathrm{d}z + \left(\frac{\partial j}{\partial t}\right)\mathrm{d}t = \theta_{\mathrm{w}}\mathrm{d}z - F_{\mathrm{w}}\mathrm{d}t \tag{15}$$

In these equations, $j(z,t)$ is a material coordinate with units (m). The j-coordinate satisfies the material balance Eq. (2) and Eq. (11) for the water, and is evaluated by integrating Eq. (15). Writing Fick's law as

$$f = -D_{\mathrm{s}}\theta_{\mathrm{w}}\frac{\partial C_{\mathrm{s}}}{\partial z} \tag{16}$$

with D_{s} ($\mathrm{m}^2\ \mathrm{s}^{-1}$) the diffusion coefficient of the solute in the pore water. Substitution of Eq. (16) in Eq. (14) again leads to a non-linear diffusion equation

$$\left(\frac{\partial C_{\mathrm{s}}}{\partial t}\right)_{j} = \frac{\partial}{\partial j}\left(D_{\mathrm{s}}\theta_{\mathrm{w}}^{2}\frac{\partial C_{\mathrm{s}}}{\partial j}\right)_{t} \tag{17}$$

2.3. *Non-reactive solute/water movement in swelling systems*

Simultaneous transfer of non-reactive solute and water in a swelling system permits a similar analysis. The material balance equations are Eq. (4) which describes the flow of water in relation to the (moving) solid (m-space),

$$\left(\frac{\partial \vartheta}{\partial t}\right)_{m} = -\left(\frac{\partial u}{\partial m}\right)_{t}$$

and

$$\left(\frac{\partial \left(C_{\mathrm{s}}\vartheta\right)}{\partial t}\right)_{m} = -\left(\frac{\partial F_{\mathrm{s}(m)}}{\partial m}\right)_{t} \tag{18}$$

which defines the material balance of solute in m-space. Eq. (18) derives from Eq. (12) noting that, on the left hand side, $C_{\mathrm{s}}\theta_{\mathrm{w}}=\theta_{\mathrm{c}}\vartheta C_{\mathrm{s}}$, and that F_{s} on the right hand side can be expanded using Eq. (13) and then Eq. (3). Differentiation, the elimination of two terms using Eq. (1), and the use of Eq. (6) then yield Eq. (18).In Eq. (18), $F_{\mathrm{s}(m)}$ is the flux of solute relative to, and with, the water moving in m-space. It is given by

$$F_{\mathrm{s}(m)} = f + C_{\mathrm{w}}u \tag{19}$$

Again, f is defined by Fick's law and u is the Darcy flux of water and, as for the first two cases, combination of Eqs. (4), (18) and (19) yields

$$\left(\frac{\partial C_{\mathrm{s}}}{\partial t}\right)_{p} = -\left(\frac{\partial f}{\partial p}\right)_{t} \tag{20}$$

with the material coordinate, p (m,t) (m) defined by

$$\mathrm{d}p = \left(\frac{\partial p}{\partial m}\right)\mathrm{d}m + \left(\frac{\partial p}{\partial t}\right)\mathrm{d}t = \vartheta\ \mathrm{d}m - u\ \mathrm{d}t \tag{21}$$

Eq. (20) appears not to have been previously formulated. It presents the material balance of the solute in a space-like coordinate that satisfies the material balance equation of the moving solution. The transfer of the solution, in turn, is formally related to m-space through Eq. (21) and thence to (physical) z-space through Eq. (5). Material balance of all components is thus respected.

Substitution of Fick's law in Eq. (18) gives rise to the diffusion equation

$$\left(\frac{\partial C_{\mathrm{s}}}{\partial t}\right)_{p} = \frac{\partial}{\partial p}\left(D_{\mathrm{s}}\theta_{\mathrm{w}}^{2}\frac{\partial C_{\mathrm{s}}}{\partial p}\right)_{t} \tag{22}$$

3. Illustrative examples

We illustrate development of the approach in terms of initial and boundary conditions defined by:

$$\begin{array}{llll} C_{\mathrm{s}} = C_{\mathrm{s(i)}}, & \theta_{\mathrm{w}} = \theta_{\mathrm{w(i)}}, & z > 0, & t = 0 \\ C_{\mathrm{s}} = C_{\mathrm{s(0)}}, & \theta_{\mathrm{w}} = \theta_{\mathrm{w(0)}}, & z = 0, & t > 0 \\ C_{\mathrm{s}} = C_{\mathrm{s(i)}}, & \theta_{\mathrm{w}} = \theta_{\mathrm{w(i)}}, & z \to \infty, & t > 0. \end{array} \tag{23}$$

These conditions would apply, for example, to a process of constant pressure filtration in a semi-infinite column, initiated at $t=0$, in which water but not solid escapes through the filter membrane at $x=0$. The conditions on C_{s} presume that at the filter membrane a step change in solution concentration exists. These conditions were realized, for example, in the experiments described in [10]. They also apply to absorption of solution by a relatively dry non-swelling soil [15].

3.1. *Water flow in swelling systems*

A convenient integration path for Eq. (5) for these conditions is:

$$m = \int_{0}^{z}\theta_{\mathrm{c}_t}\mathrm{d}z - \int_{0}^{t}F_{\mathrm{c}_{z=0}}\mathrm{d}t \tag{24}$$

But $F_{\mathrm{c}}=0$ at $z=0$, so m is the cumulative volume of solid, per unit area of cross section, measured away from the filter membrane. m then replaces z in Eq. (23) and the Boltzmann substitution $M=mt^{-1/2}$ eliminates explicit appearance of m and t from the experimental conditions *on the water*, which become

$$\begin{array}{lll} \vartheta = \vartheta_{\mathrm{i}}, & \left(\theta_{\mathrm{w}} = \theta_{\mathrm{w(i)}}\right), & M \to \infty \\ \vartheta = \vartheta_{0}, & \left(\theta_{\mathrm{w}} = \theta_{\mathrm{w(0)}}\right), & M = 0 \end{array} \tag{25}$$

in consistent dimensions, and Eq. (10) becomes the ordinary differential equation

$$\frac{\mathrm{d}}{\mathrm{d}M}\left(D\left(\vartheta\right)\theta_{\mathrm{c}}\frac{\mathrm{d}\vartheta}{\mathrm{d}M}\right) + \frac{M}{2}\left(\frac{\mathrm{d}\vartheta}{\mathrm{d}M}\right) = 0 \tag{26}$$

with

$$M = \int_{0}^{Z}\theta_{\mathrm{c}}\mathrm{d}Z \tag{27}$$

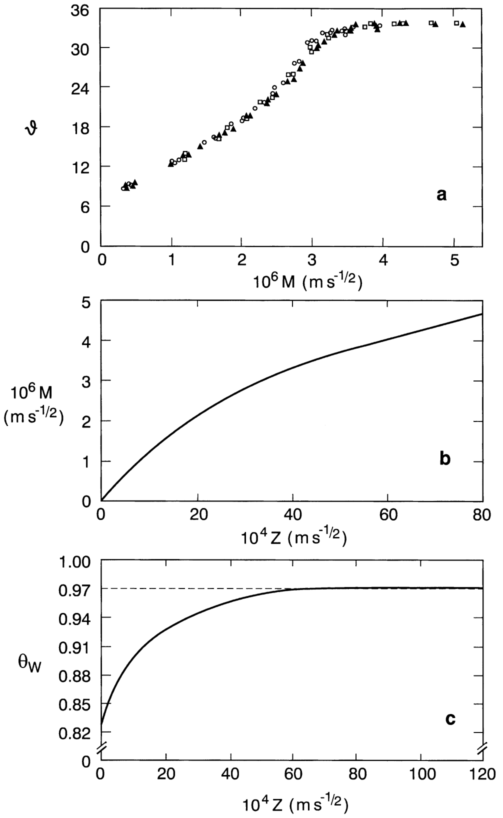

Fig. 1. Water content profiles observed during constant pressure filtration of Wyoming bentonite and expressed (as they were originally derived) in material space (a). Fig. 1b shows the relation between the material (M) and physical (Z) coordinates derived from the data of Fig. 1a and Fig. 1c shows the volume fraction of the water expressed as a function of $Z=zt^{-1/2}$. Further detail is provided in the text.

and $Z=zt^{-1/2}$. If Eq. (26) is valid and conditions Eq. (25) are realized, then $\vartheta(M)$ will be unique.

Fig. 1 shows water content profiles observed during constant pressure filtration of Wyoming bentonite [16]. These experiments explored the effects of solution concentration and temperature on filtration behaviour and the permeability and effective stress characteristics of this clay. The filtering clay columns were destructively sampled a range of elapsed times. Fig. 1a shows $\vartheta(M)$, Fig. 1b shows $Z(M)$ and Fig. 1c shows $\theta_w(Z)$.

In this example, the initial experimental data were determined in m-space. This is because it is easier and more accurate to measure weights of water and oven dry solid during fine serial sectioning, which often involves samples less than 1 mm thick, than it is to measure physical distance and volume fractions in z-space. Thus Fig. 1b is derived, for this saturated system, from Fig. 1a using (cf. Eq. (27))

$$Z=\int_0^M (1+\vartheta)^{-1}\,\mathrm{d}M \tag{28}$$

while Fig. 1c derives from Fig. 1a and Fig. 1b and noting that $\theta_w=\vartheta/(1+\vartheta)$.

The m-coordinate has the benefit that the mathematics in m-space is much simplified when compared with development in z-space [17,18] because we deal with a diffusion equation rather than the integro-differential equation required explicitly to account for drift of the particles.

Finally, because the analysis is strain independent, it obviates errors in interpretation of data. For example, the integrals under the curves in Fig. 1a and Fig. 1c are unequal despite the fact that in both coordinate systems, similarity is preserved. Specifically, the cumulative outflow $S(\vartheta_i,\vartheta_0)$ (m s$^{-1/2}$) is given [19] by

$$S(\vartheta_i,\vartheta_0)=\int_{\vartheta_0}^{\vartheta_i} M\,\mathrm{d}\vartheta=\theta_c^{-1}\int_{\theta_{w0}}^{\theta_{wi}} Z\,\mathrm{d}\theta_w \tag{29}$$

Thus, an error proportional to θ_c arises in the estimation of the flux of water if the movement of the solid in physical space is ignored and the cumulative flow is simply based on the integral in z-space. That possibility for error does not arise in material space.

3.2. Non-reactive solute flow in non-swelling systems

We illustrate evaluation of the j-coordinate for the case of absorption of solute by an initially relatively dry soil from a solution source at constant water potential. Integration of Eq. (15) then yields

$$j=\int_0^z \theta_{w_t}\,\mathrm{d}z-\int_0^t F_{w_{x=0}}\,\mathrm{d}t \tag{30}$$

with the second term on the right, the cumulative amount of water that crosses $z=0$ [7]. $j=0$ is a notional moving interface between invading water and that originally present, were displacement of the latter by the former, perfect. In terms of the initial and boundary conditions Eq. (23), $j=0$ identifies a step change in C_s. Thus

$$\begin{aligned} &C_s=C_{s(i)}, && j>0,\quad t=0\\ &C_s=C_{s(0)}, && j<0,\quad t=0,\quad \text{and}\\ &\int_{C_{s(i)}}^{C_{s(0)}} j\,\mathrm{d}C_s=0, && t>0 \end{aligned} \tag{31}$$

and we presume the system to be effectively doubly semi-infinite with preservation of the total amount of solute reflected in the integral in Eq. (31).

We note again that Z eliminates explicit appearance of z and t in the flow equation for the water and conditions (Eq. (23)) and we use the reduced coordinates, Z and $J=jt^{-1/2}$. In this system, Eq. (17) and Eq. (31) become

$$\frac{\mathrm{d}}{\mathrm{d}J}\left(D_s\theta_w^2\frac{\mathrm{d}C_s}{\mathrm{d}J}\right)+\frac{J}{2}\left(\frac{\mathrm{d}C_s}{\mathrm{d}J}\right)=0 \tag{32}$$

and

$$\begin{aligned} &C_s=C_{s(i)}, && J\to+\infty\\ &C_s=C_{s(0)} && J\to-\infty,\quad \text{and}\\ &\int_{C_{s(i)}}^{C_{s(0)}} J\,\mathrm{d}C_s=0 \end{aligned} \tag{33}$$

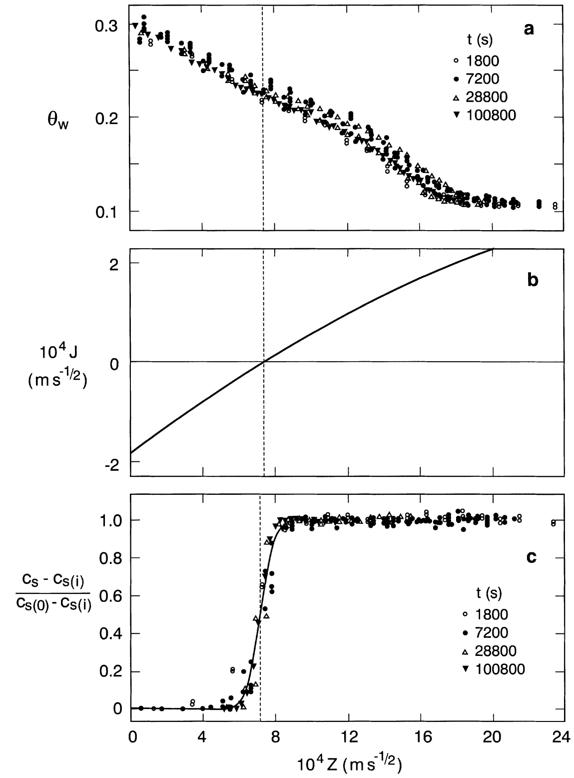

Fig. 2. Water and salt concentration profiles observed during absorption of solution by an initially relatively dry soil. Fig. 2a shows the water content and the way it scales according to Z for experiments terminated at different times. Fig. 2b shows the relation between the (moving) material J-coordinate, and the physical Z-coordinates. Fig. 2c shows the normalised solution concentrations and the way the solute front in these experiments corresponds to the piston front where J=0.

with

$$J = \int_0^Z \theta_w \mathrm{d}Z - S\left(\theta_{w(i)}, \theta_{w(0)}\right) \tag{34}$$

while the water flow remains governed by Eq. (25) and Eq. (26).

Fig. 2a shows the distribution of water during absorption into a relatively dry non-swelling soil and illustrates the use of the Boltzmann substitution. Fig. 2b shows the relation between the Z and J. $J = 0$ corresponds to this piston front (in Z-space) and solute disperses about it. Fig. 2c illustrates this phenomenon in Z-space although, strictly speaking, the units of concentration and space in this figure are inconsistent because C, in Z-space, should be expressed per unit volume of the system, rather than per unit volume of solution as is appropriate in J-space.

Again, the mathematics are much simplified, particularly when unsteady water flow is considered and material balance implicitly retained if the correct units are used.

3.3. Non-reactive solute/water and clay movement

This situation might arise, for example, in a process of constant pressure filtration, initiated at t=0, in which water but not solid escapes through the filter membrane at x=0. The conditions on C_w presume that at the filter membrane a step change in solution concentration exists. These conditions were realized, for example, in the experiments described in [10]. It transpires that the Boltzmann substitution again permits use of the reduced coordinates $Z = zt^{-1/2}$, $M = mt^{-1/2}$ for these conditions, and we may introduce a reduced coordinate $P = pt^{-1/2}$ which eliminates p and t from Eq. (22) and Eq. (23) expressed in p-space using Eq. (21).

Eqs. (22) and (23) then become

$$\frac{\mathrm{d}}{\mathrm{d}P}\left(D_\mathrm{s}\theta_\mathrm{w}^2 \frac{\mathrm{d}C_\mathrm{s}}{\mathrm{d}P}\right) + \frac{P}{2}\frac{\mathrm{d}C_\mathrm{s}}{\mathrm{d}P} = 0 \tag{35}$$

and

$$\begin{array}{lll} C_\mathrm{s} = C_{\mathrm{s(i)}}, & \theta_\mathrm{w} = \theta_{\mathrm{w(i)}}, & P > 0 \\ C_\mathrm{s} = C_{\mathrm{s(0)}}, & \theta_\mathrm{w} = \theta_{\mathrm{w(0)}}, & P = -S \end{array} \tag{36}$$

with P defined in terms of the water distribution in M-space by

$$P = \int_0^M \vartheta \mathrm{d}M - S\left(\vartheta_{\mathrm{w(i)}}, \vartheta_{\mathrm{w(0)}}\right) \tag{37}$$

If Eq. (10) is valid, and Eq. (23) realized and if Eq. (27) is valid and conditions Eq. (35) and Eq. (36) are realized, then C_s (P) must be unique. Thus, evolutionary profiles of water content and solute concentration test the approach and its assumptions. They also permit estimation of $D(u,\vartheta)$. Alternatively, if $D(u,\vartheta)$ is known, the profiles of $C_\mathrm{s}(P)$ can be calculated for conditions Eq. (28) and Eq. (29).

4. Concluding remarks

Material coordinates are useful to describe 1-dimensional unsteady flow of water in swelling systems, solute with water in unsaturated flow in non-swelling systems and solute, water and solid in swelling systems. They are formulated in the same way, they result in essentially the same diffusion-like flow equation and they permit similar types of solution. Application of the approach to 2- and 3-dimensional solute/water flow in non-swelling soils is straightforward. Use of material coordinates to describe water flow in 2- and 3-dimensional systems remains a challenge, however, although the structure of the problem often permits useful simplification [20].

Illustrations here relate to experimental conditions that permit use of the Boltzmann substitution. This is not a necessary condition for use of these coordinates [8]; it does however offer a useful space/time scaling test of the flow equations and of the realization of the experimental conditions. It also provides a useful basis for measurement, for example, of $D_m(\vartheta)$ [13]. The approach may also be used in unsaturated swelling systems [20] and where gravity and overburden effects are significant [21].

While the approach here is illustrative and restricted to non-reactive solutes, its analogue in unsaturated non-swelling soil water flow has been extended to cases where the solute participates in exchange and sorption reactions and, while these reactions are often complicated, the material coordinate remains useful. Papers [22–26] illustrate examples of hydrodynamic dispersion and chemical reaction in rigid systems. The physical consequences of chemical reaction during solute flow in colloidal systems has yet to be systematically explored [10,11].

References

[1] F.M. Tiller, The role of porosity in filtration, Chem. Eng. Prog. 51 (1955) 282.

[2] D.E. Smiles, A theory of constant pressure filtration, Chem. Eng. Sci. 25 (1970) 985.

[3] M. Shirato, H. Kato, K. Kobayashi, et al., Analysis of settling of thick slurries due to consolidation, J. Chem. Eng. Jpn. 3 (1970) 98.

[4] K. Atsumi, T Akiyama, S. Miyagawa, Expression of thick slurry of titanium dioxide in water, J. Chem. Eng. Jpn. 6 (1973) 236.

[5] M. Willis, I. Tosun, A rigorous cake filtration theory, Chem. Eng. Sci. 35 (1980) 2427.

[6] M. Shirato, T. Murase, M. Iwata, T. Kurita, Principles of expression and design of membrane compression type filter press operation, in: N.P. Cherimisinoff (Ed.), Encyclopedia of Fluid Mechanics, vol. V, Slurry Flow Technology, Gulf Publishing, Houston, TX, 1986.

[7] I. Tosun, Formulation of cake filtration, Chem. Eng. Sci. 41 (1986) 2563.

[8] D.E. Smiles, K.M. Perroux, S.J. Zegelin, et al., Hydrodynamic dispersion during constant rate absorption of water by soil, Soil Sci. Soc. Am. J. 45 (1981) 453.

[9] J.L. Wilson, L.W. Gelhar, Analysis of longitudinal dispersion in unsaturated flow 1, the analytical method, Water Resour. Res. 17 (1981) 122.

[10] D.E. Smiles, J.M. Kirby, I.P. Little, Physico-chemical change in sodium bentonite during filtration through plaster-of-Paris, Chem. Eng. Sci. 51 (1996) 3647.

[11] D.J. Jensen, C.J. Radke, Caesium and strontium diffusion through sodium montmorillonite at elevated temperature, J. Soil Sci. 59 (1988) 53.

[12] D.E. Smiles, Material coordinates and solute movement in consolidating clay, Chem. Eng. Sci. 55 (2000) 773.

[13] D. Zaslavsky, Saturated and unsaturated flow equation in an unstable medium, Soil Sci. 98 (1964) 317.

[14] D.E. Smiles, Principles of constant pressure filtration, in: N.P. Cheremisinoff (Ed.), Encyclopedia of Fluid Mechanics, vol. V, Slurry Flow Technology, Gulf Publishing, Houston, TX, 1986.

[15] D.E. Smiles, J.R. Philip, Solute transport during absorption of water by soil: laboratory studies and their practical implications, Soil Sci. Soc. Am. J. 42 (1978) 537.

[16] D.E. Smiles, C.J. Barnes, W.R. Gardner, Water relations of saturated bentonite: some effects of temperature and solution salt concentration, Soil Sci. Soc. Am. J. 49 (1985) 66.

[17] J.R. Philip, Kinetics of sorption and volume change in clay-colloid pastes, Austr. J. Soil Res. 6 (1986) 249.

[18] R.J. Wakeman, Numerical integration of the differential equations describing the formation of and flow in compressible filter cakes, Trans. Inst. Chem. Eng. 56 (1978) 258.

[19] D.E. Smiles, Water balance in swelling materials: some comments, Austr. J. Soil Res. 35 (1997) 1143.

[20] D.E. Smiles, Centrifugal filtration of particulate systems, Chem. Eng. Sci. 54 (1999) 21.

[21] J.R. Philip, D.E. Smiles, Kinetics of sorption and volume change in three-component systems, Austr. J. Soil Res. 7 (1969) 1.

[22] J.R. Philip, Flow in porous media, in: E. Becker, G.K. Mikhailov (Eds.), Proceedings of the 13th International Congress on Theoretical and Applied Mechanics, Moscow, Springer–Verlag, Berlin, 1973, pp. 279.

[23] W.J. Bond, I.R. Philips, Approximate solutions for cation transport during unsteady, unsaturated soil water flow, Water Resour. Res. 26 (1990) 2195.

[24] W.J. Bond, I.R. Philips, Ion transport during unsteady water flow in an unsaturated clay soil, Soil Sci. Soc. Am. J. 54 (1990) 636.

[25] R.S. Mansell, W.J. Bond, S.A. Bloom, Simulating cation transport during water flow in soil: two approaches, Soil Sci. Soc. Am. J. 57 (1993) 3.

[26] A.J. Valocchi, R.L. Street, P.V. Roberts, Transport of ion-exchanging solutes in groundwater: chromatographic theory and field simulation, Water Resour. Res. 17 (1981) 1517.