



Diffusion through confined media at variable concentrations in reservoirs

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ABSTRACT

The problem of transient linear 1D diffusion with mass-transfer limitations (boundary layers) at the medium boundaries and variable diffusant concentrations in both perfectly stirred reservoirs is solved in terms of Fourier transforms. This novel solution is especially relevant to the interpretation of measurements of diffusion of adsorbing radio-nuclides in compacted clays where porous filters are routinely used to confine the swelling clay. An analytical expression is obtained for the break-through time with a due account for the mass-transfer limitations at the medium boundaries. An analysis is carried out of the influence of finite inlet volume on the time evolution of diffusant flux into the outlet reservoir. A simple “renormalization” procedure is put forward to make corrections for the decrease in the inlet concentration, which makes applicable the classical procedure of interpretation in terms of stationary flux and break-through time. It is shown that this “renormalization” procedure is fairly accurate in the case of relatively small absolute sorption capacities of medium (as compared to the inlet reservoir), but its accuracy deteriorates with an increase in this parameter. Several examples are considered for the application of these approaches to the interpretation of experimental data on the diffusion of traces of radioactive ²²Na through compacted sodium montmorillonite.

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1. Introduction

Compacted clays are often used as fine-grained barrier materials for the isolation of waste disposal sites [1,2]. Because the hydraulic permeability is usually very low in such materials (typically: $k_f < 10^{-11}$ m/s for a sand/bentonite mixture with a bentonite content >50% [3]), the transport of pollutants in such media occurs via molecular diffusion. Consequently, the diffusion properties of clays have to be characterized in order to be able to evaluate their barrier function. An excellent overview of different laboratory diffusion testing techniques for waste disposal is given in [4]. Practical applications on bentonite are given in a number of publications such as [5–9]. Examples for argillaceous rocks can be found in [10–14]. In the case of through-diffusion or in-diffusion from a tracer solution reservoir, the need for confining the samples between porous filter plates is evident when studying diffusion in materials that have swelling properties such as bentonite [15,16] or deteriorate in contact with water such as Opalinus Clay [17]. The use of filter plates at the boundaries, however, can lead to mass-transfer limitations. As long as the diffusion permeabilities of the porous filters are much larger than the diffusion permeabil-

ity of the clay, the mass-transfer limitations due to the filters can be neglected and the well-known solutions of the diffusion equation can be used [4,18]. However, when the filters have diffusion permeabilities comparable to or lower than that of the clay sample, mass-transfer limitations at the clay boundaries have to be taken into account. Put [19] obtained a Laplace-transform solution for taking into account the effect of filters in the case of through-diffusion measurements. However, he assumed the diffusant concentration in the inlet reservoir to be constant.

The sorption capacities of compacted clays with respect to cationic radio-nuclides are often quite high [4,15,16]. Accordingly, considerable amounts of diffusant are adsorbed by the clay in the course of diffusion experiments. To have the diffusant concentration in the inlet reservoir approximately constant irrespective of that, either the volume of this reservoir need to be very large or certain amounts of diffusant have to be periodically added to it in order to offset the losses due to the adsorption. Both of those options are technically difficult to implement, in particular, due to the fact that many radio-tracers are quite expensive. Therefore, the constancy of diffusant concentration in the inlet reservoir is practically never achieved in experimental practice.

The variation of diffusant concentration in both feed and receiving reservoirs was first taken into account by Spacek and Kubin [20]. However, they disregarded the mass-transfer limitations at the medium boundaries. The latter (as well as the variable diffu-

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sant concentration in the inlet reservoir) were accounted for by Jahnke [21], but only in the limiting case of in-diffusion (infinitely thick medium). We are unaware of attempts to account for the mass-transfer limitations and the variable reservoir concentrations occurring simultaneously for finite medium thicknesses.

We shall obtain a general solution to the problem of linear 1D diffusion with mass-transfer limitations at the medium boundaries and with variable diffusant concentrations in both perfectly stirred reservoirs in terms of Fourier transforms. This solution will be used to derive a new analytical expression for the breakthrough time with a due account of mass-transfer limitations. Besides that, it will be employed to check the scope of applicability of a flux renormalization procedure allowing for a correction for the decrease of diffusant concentration in the inlet reservoir. The utility of our theoretical approaches will be illustrated by using the results of measurements of diffusion of radioactive ^{22}Na through highly compacted sodium montmorillonite equilibrated with NaClO_4 solutions of several ionic strengths reported in [22].

2. Theory

The basis is the classical equation of non-steady-state diffusion [18]:

$$\alpha \frac{\partial c(x, t)}{\partial t} = D_e \frac{\partial^2 c(x, t)}{\partial x^2} \quad (1)$$

where c is the concentration of “free” (non-adsorbed) diffusant, α is the so-called rock capacity factor (defined as dimensionless distribution coefficient between the medium and an equilibrium solution), and D_e is the effective diffusion coefficient in the medium. The coefficients are assumed to be independent of diffusant concentration (linear sorption). Further, it is supposed that the boundary layers have negligible sorption capacities; therefore the concentration profiles inside them are linear anytime.

It should be stressed that our analysis is primarily related to the experimental studies of diffusion of trace amount of radio-nuclides. Due to the very low concentrations of radio-tracers (as compared to other solutes), the state of thermodynamic equilibrium of the system is practically not perturbed by the introduction of diffusant. Accordingly, there are no osmotic flows in the system, and usually the sorption can be considered linear, indeed, despite, for example, the considerable impact of electrostatic phenomena on the diffusion in clays.

2.1. Boundary conditions and material balances

It is assumed that the solutions in the reservoirs are perfectly stirred. Therefore, the solute fluxes at the medium boundaries are directly proportional to the concentration differences across the corresponding boundary layers, i.e.

$$-D_e \left. \frac{\partial c}{\partial x} \right|_{x=0} = P_b(c_1(t) - c(0, t)) \quad (2)$$

$$-D_e \left. \frac{\partial c}{\partial x} \right|_{x=L} = P_b(c(L, t) - c_2(t)) \quad (3)$$

where P_b is the diffusion permeability of the boundary layers (assumed to be the same for both of them and defined as the effective diffusion coefficient over the thickness), $c_{1,2}(t)$ are the solute concentrations in the corresponding reservoirs, the origin of the space variable x is chosen at the left medium boundary, and L is

the co-ordinate of the right medium boundary.¹ The conditions of material balance are that the rates of changes in the diffusant concentrations in the reservoirs are proportional to the solute fluxes in and out of the medium (remember that the sorption capacities of the boundary layers are assumed to be negligible therefore the flux into a boundary layer is equal to the flux out of it).

$$\frac{dc_1(t)}{dt} = \frac{SP_b}{V_1}(c(0, t) - c_1(t)) \quad (4)$$

$$\frac{dc_2(t)}{dt} = \frac{SP_b}{V_2}(c(L, t) - c_2(t)) \quad (5)$$

where S is the cross-sectional area, and $V_{1,2}$ are the volumes of the corresponding reservoirs.

2.2. Characteristic lengths and times in the system

In the classical analysis, which disregards both the mass-transfer limitations and the concentration variation in the reservoirs, there is only one characteristic length in the system, namely, the thickness of the medium. In our analysis, besides the impact of mass-transfer limitations, we shall mainly concentrate our attention on the role of finite volume of the inlet reservoir, while considering the outlet reservoir infinitely large (as it is mostly the case in experimental practice; see below for the details). Therefore, there are three characteristic lengths in the system, namely, L , D_e/P_b , and V_1/S . The second one is the thickness of a medium layer whose diffusion permeability would be equal to that of the boundary layer. The third one is the effective thickness of the inlet reservoir. The choice of characteristic length (and, accordingly, of characteristic time), is a matter of convenience and depends on the emphases of analysis. If we select this characteristic length

$$l_c \equiv \frac{D_e}{P_b} \quad (6)$$

the corresponding characteristic time is

$$t_{ch} \equiv \frac{\alpha D_e}{P_b^2} \quad (7)$$

This time is needed for the diffusant concentration at the boundary between the medium and the inlet boundary layer to increase from the initial value to about half the value in the inlet reservoir in the particular case of infinitely thick medium and infinitely large inlet reservoir.

The concentration is scaled on the initial concentration in the inlet reservoir. In the dimensionless variables, $\xi \equiv x/l_c$, $\tau \equiv t/t_{ch}$, Eq. (1) takes this form:

$$\frac{\partial c(\xi, \tau)}{\partial \tau} = \frac{\partial^2 c(\xi, \tau)}{\partial \xi^2} \quad (8)$$

The boundary and material balance conditions transform to this:

$$-\left. \frac{\partial c(\xi, \tau)}{\partial \xi} \right|_{\xi=0} = c_1(\tau) - c(0, \tau) \quad (9)$$

$$-\left. \frac{\partial c(\xi, \tau)}{\partial \xi} \right|_{\xi=h} = c(h, \tau) - c_2(\tau) \quad (10)$$

$$\frac{dc_1(\tau)}{d\tau} = k_1(c(0, \tau) - c_1(\tau)) \quad (11)$$

¹ Since the sorption capacity of boundary layers is assumed to be negligible, the concentration profiles inside them are always linear. Therefore, they can be characterized by a single parameter, namely, the diffusion permeability, and their thickness is formally considered infinitely small.

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