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Journal of Contaminant Hydrology 93 (2007) 304–315

JOURNAL OF
Contaminant
Hydrology

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Predictive modelling of dispersion controlled reactive plumes at the laboratory-scale

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Received 25 July 2005; received in revised form 29 March 2007; accepted 13 April 2007
Available online 5 May 2007

Abstract

A model-based interpretation of laboratory-scale experimental data is presented. Hydrolysis experiments carried out using thin glass tanks filled with glass beads to construct a hypothetical and inert, homogeneous porous medium were analysed using a 2D numerical model. A new empirical formula, based upon results for non-reactive (tracer) experiments is used to calculate transversal dispersivity values for a range of grain sizes and any flow velocities. Combined with effective diffusion coefficients calculated from Stokes–Einstein type equations, plume lengths arising from mixing between two solutes can be predicted accurately using numerical modelling techniques. Moreover, pH and ion concentration profiles lateral to the direction of flow of the mixing species can be determined at any given point downstream, without the need for result fitting. In our case, this approach does not lead to overpredictions of lateral mixing, as previously reported when using parameters derived from non-reactive tracer experiments to describe reactive solute transport. The theory is based on the assumption of medium homogeneity.

Keywords: Transversal dispersivity; Plume length; Mixing; Dilution; Mechanical dispersion; Molecular diffusion

1. Introduction

In many cases, transversal hydrodynamic dispersion is thought to be the controlling mechanism for the attenuation of organic and other contaminants (Cirpka et al., 1999; Grathwohl et al., 2000). For example, the length of steady-state contaminant plumes of biodegradable, oxidisable organic compounds was found to be controlled by transversal mixing of electron acceptors, or growth-limiting nutrients across the plume fringe (Grathwohl et al., 2000; Ham et al., 2004). In contrast, longitudinal dispersion was shown to only influence transient plume behaviour (Ham et al., 2004), in particular at the downstream end of a developing plume (Cirpka et al., 2006).

Both transversal and, to an even greater extent, longitudinal dispersion have been reported to be scale-dependent mechanisms (Sturman et al., 1955; Kitanidis, 1994; Dykaar and Kitanidis, 1996; Kapoor and Kitanidis, 1998) and dispersivity values employed to characterise, for example, plume behaviour, often reflects the scale of heterogeneity of the porous medium (Sturman et al., 1955; Huang, 2002). Given the inherent difficulties of accurately quantifying the transversal dispersivity α_t at

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doi:10.1016/j.jconhyd.2007.04.002

the field-scale, α_t has for simplicity in many practical cases been assumed to be a certain fraction (e.g., approximately one tenth (Grane and Gardner, 1961)) of the longitudinal dispersivity values, which at the plume-scale (Cirpka et al., 1999) largely characterises macro-scale dispersion. However, when considering reactive solute transport, for example in the context of field-scale biodegradation problems, the relevant scale of mixing that controls overall reaction rates is the pore-scale (Bear, 1972; Cirpka et al., 1999; Cirpka and Kitanidis, 2000). Consequently, if hydrodynamic dispersion coefficients that represent macro-scale dispersion are used to quantify the transport of reacting solutes, this results in an overestimation of mixing (Cirpka et al., 1999) and therefore an overprediction of reaction rates.

To date, no modelling approach that could fully get around those scaling-issues has been proposed. To overcome this problem, several laboratory studies have been initiated in attempts to study transport and reactive processes at a fundamental level and under controlled conditions. For example, Gramling et al. (2002) studied the one-dimensional transport, mixing and reactions of CuSO4 and EDTA^{4-} in a translucent chamber filled with cryolite sand. They found that if they used previously derived dispersion coefficients (from non-reactive experiments) to predict reactive transport behaviour, the concentrations of the formed CuEDTA^{2-} were overestimated by up to 20%. Similarly, an earlier modelling study to investigate *in-situ* biorestoration of chlorinated aliphatics by Semprini and McCarty (1991), shows that reactive mixing was overestimated when dispersivity values from non-reactive tracer experiments were used in model simulations. In contrast, Huang et al. (2003), in tracer experiments, found that experimental data could only be fitted by a numerical model when dispersivity values were increased by a factor of three for the reactive cases; the authors concluding that biomass blocking some pore spaces could increase the tortuosity of the medium.

The present paper reports the results from a series of laboratory-scale tank experiments and the model-based interpretation of the experimental data. The research objectives are to determine whether values of the transversal dispersivity α_t obtained from non-reactive transport experiments can or cannot be used to predict reactive solute transport and in addition establish the contribution of mechanical dispersion to solute mixing. Since at the laboratory-scale the role of molecular diffusion may be as or even more important than mechanical transversal dispersion in influencing lateral plume development (Huang et al., 2003), an accurate quantification of the process and its contribution to the mixing is essential for the interpretation of the experimental data. Therefore we also briefly review the theory of multi-component diffusion in the context of the experiments analysed here.

2. General theory

The generalised form of the macroscopic advection–dispersion equation (ADE) for a tracer of concentration C, with units $[\mathrm{M\,L^{-3}}]$ can be written

$$\frac{\partial C}{\partial t} + V \cdot \mathrm{grad}C = \mathrm{div}(D \cdot \mathrm{grad}C) \tag{1}$$

where t is the time, V is the mean pore velocity with units $[\mathrm{LT^{-1}}]$ and D is the dispersion tensor with units $[\mathrm{L^2T^{-1}}]$. Eq. (1) is valid for steady-state flow only, i.e. $\nabla V=0$. Depending on the role played by molecular diffusion D_m, the dispersion tensor D is usually assumed to be proportional to some power of the velocity between 1 and 2 (Scheidegger, 1957; Bear, 1972). This power can be taken as 1 when considering only the average linear velocity in a porous medium (Bear and Todd, 1960), i.e., the dispersion tensor is directly proportional to the average linear velocity. In a homogeneous and isotropic two-dimensional uniform flow field, where there is no sorption, the macroscopic ADE for a single species k can be written

$$\varepsilon\frac{\partial C(k)}{\partial t} + q_x\frac{\partial C(k)}{\partial x} - D_l\frac{\partial^2 C(k)}{\partial x^2} - D_t\frac{\partial^2 C(k)}{\partial y^2} + r^k = 0, \tag{2}$$

where ϵ is the porosity of the porous medium, C is the concentration of species k, q_x is the specific discharge, D_l and D_t are the longitudinal and transversal dispersion coefficients respectively, and r is a reaction (source/sink) term.

2.1. Classical form of the dispersion tensor

Typically, Fick's Law is used to characterise diffusive transport of ionic species in porous materials (Crank, 1964) and generally works well when applied to experimental data. When there is appreciable transversal molecular diffusion, the transversal dispersion coefficient D_t is considered as the sum of the effective molecular diffusion coefficient D_m and the product of transversal dispersivity α_t and seepage velocity $v=q_x/\epsilon$, i.e.

$$D_t = D_m + \alpha_t|v|, \tag{3}$$

where D_m is a function of porous media geometry and temperature. Some authors would argue that the Fickian