Microporous and Mesoporous Materials 185 (2014) 51–60

Contents lists available at ScienceDirect

Microporous and Mesoporous Materials

journal homepage: www.elsevier.com/locate/micromeso

Discrete modelling of contaminant diffusion in porous media with sorption ☆

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ARTICLE INFO

Article history:
Received 29 May 2013
Received in revised form 27 August 2013
Accepted 29 September 2013
Available online 7 October 2013

Keywords:
Bentonite
Diffusion
Sorption
Pore network
Transient analysis

ABSTRACT

A meso-scale model for diffusion of foreign species through porous media is proposed. The model considers diffusion as a continuous process operating on a discrete geometrical structure dictated by the pore size distribution. Local diffusivities and hence pore space connectivity are dependent on the size of the diffusing species and the sorption of those species onto the pore walls. The bulk diffusivity of the medium has been analysed to consider the effects of pore structure alone and in combination with sorption. The chosen medium is bentonite, which is being considered for use as a barrier to radionuclide transport in future deep geological repositories for nuclear waste. Results for transient diffusion of U(VI)-complex through bentonite are presented and very good agreement with experiments is demonstrated. Results for diffusion of larger chemical complexes are also presented to illustrate the effect of reduced pore space connectivity on steady-state and transient transport parameters. Diffusion of larger complexes can be used for experimental validation of the model. The proposed methodology can be used for any micro- and meso-porous material with known distribution of pore sizes. It can be extended to other pore space changing mechanisms, in addition to sorption, to derive mechanism-based evolution laws for the transport parameters of porous media.

1. Introduction

Pore network models (PNM) of mass transport through porous media are an attractive way to analyse the effects of changing pore space structure on macroscopic transport coefficients, such as permeability [1,2] and diffusivity [3,4]. These transport coefficients are required for engineering analyses using, for example, finite element or finite difference methods. The analysis of changes in transport coefficients with changes in the underlying structure can, using pore network models, provide mechanistic as opposed to phenomenological evolution laws for engineering analyses.

Pore network models idealise the medium as a set of pores, some of which are connected by throats or mass conduits, in which transport is allowed only through the system of throats. In ideal circumstances, constructing a PNM requires a wide range of microstructural information, including porosity, size distribution of pores, size distribution of throats, average pore coordination, and the coordination spectrum: the fraction of pores coordinated by different numbers of throats [5]. For macro-porous materials the required parameters are readily obtainable with current experimental techniques, such as computed X-ray tomography [6,7]. For micro- and meso-porous media the distribution of pore sizes can usually be determined but the resolution of the experimental techniques tends not to be sufficient to segment all the throats and calculate their sizes. However, valuable information on the connectivity between resolved pores, the presence of throats in the PNM sense, is available indirectly from macroscopically measured mass transport. A principal objective of this work is to develop a pore network model which can be constructed with the limited microstructural information available for micro- and meso-porous media; in this case the distribution of pore sizes alone. The pore network model is based on a recently proposed network architecture [5] capable of describing rich sets of pore coordination spectra conforming to macro-porous datasets [6,7].

We have chosen to illustrate the development of our pore network model by considering the properties of bentonite; a clay displaying pore sizes ranging between sub-nanometres and several hundred nanometres [8]. Although the micro- and meso-pores (<50 nm) in this material are roughly 20% of all pores, they have a pronounced influence on the mass transport. As a result, bentonite exhibits very low permeability and the principal mass transport mechanism is diffusion [9]. Bentonite is being considered as a

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http://dx.doi.org/10.1016/j.micromeso.2013.09.038

backfill material around containers of high-level radioactive waste in most of the current designs for deep geological disposal of nuclear wastes. It is planned to serve as a critical barrier to radionuclide transport between degrading containers and host rock over very long time scales. It is therefore of substantial interest to repository designers and risk assessors to be able to predict diffusivity of radionuclides in bentonite, particularly when the pore space evolves with time as a result of environmental factors.

Sorption of diffusing species changes the pore space in bentonite and may have a significant beneficial impact on the long-term diffusivity [10,11]. In this work we will differentiate between the macroscopic diffusivity of the system with and without sorption [12]. The latter is usually referred to as the effective diffusivity of the medium, D_e, and depends on the pore space structure alone. The former is referred to as the apparent diffusivity, D_a, and depends on the sorption kinetics in addition to the pore space structure. A second objective of the work is to develop the model to account for sorption effects and demonstrate its use in deriving time-dependent changes in the mass transport. Factors that could change the pore space to increase diffusivity, such as corrosion or mechanical damage/micro-cracking, are also of substantial interest for the long-term repository behaviour. These are not considered here, but are the subject of other investigations.

In view of the role of bentonite as a barrier to radionuclide transport, our focus is on the diffusion of a specific U(VI) complex. Experimental diffusivity data of this complex in bentonite is available from the literature and will provide some of the validation of our model. This complex is smaller than the experimentally measured pore space and percolates easily through the synthetic pore network model. In this case nearly all network pores are fully coordinated. The model establishes a link between the size of the diffusing particles and the apparent network connectivity. To study the effect of reduced pore connectivity, analysis of diffusion of a larger species is also performed. It is shown further how the small-scale numerical model can be used to perform realistic transient diffusion analysis using appropriately derived film coefficients for model boundaries.

2. Model description

2.1. Discrete geometrical space for diffusion

The system of pores in a porous medium can be considered as a set of voids of variable size randomly distributed in space. The coordination of each void with neighbouring voids, or the potential pathways for mass transport, can be determined by construction of the Voronoi diagram around all voids [13]. This tessellates the space into polyhedral cells with one void per cell. The neighbours of a particular void are the voids residing in cells having common faces with the cell of the void of interest. Thus a void has as many neighbours, and hence potential mass transport channels, as the number of faces of its cell.

The process of tessellation can be used to construct pore networks from reconstructed 3D-images of a particular sample of a porous medium [14]. However, networks built this way are irregular and quite specific to the imaged sample. We prefer to generalise the problem to avoid this sample-dependency and allow ourselves to scale the results up to sizes relevant to engineers. To do this, the network has to be homogenised in some way to consider the voids to reside in identical cells. Such cells need to fill the 3D space compactly, and be as close to the "average" Voronoi polyhedron as possible in a topological sense. Monte Carlo studies of tessellations around random systems of points have provided the statistics of Voronoi polyhedral cells [15]. From there it can be judged that the regular space-filling polyhedron closest to the average cell in an arbitrary spatial distribution of voids is the so called truncated octahedron, or Kelvin solid.

A novel architecture for pore network construction based on the Kelvin solid has been recently proposed and applied to permeability analyses of porous media with known pore and throat size distributions [5]. The discrete regular cellular network based around the pores is adopted in this work and developed further to construct models for diffusion when only knowledge of the pore sizes is available – a situation typical for micro- and meso-porous materials.

The model geometry is illustrated in Fig. 1. A segment of the cellular tessellation of 3D space is shown in Fig. 1a, together with pores of arbitrary size residing at the cell centres. The pores are thought of as spherical containers with volumes dictated by the experimentally obtained pore size distribution, as described below. The entire porosity of the medium is assigned to the pores. Potential pathways for mass transport in this system of pores are depicted in Fig. 1b as cylinders. These represent throats of variable diffusivities, which may be zero, dictated by the sizes of the coordinated pores and the size of the diffusing species, as described later. The throats are volume-less conduits, allowing mass transport *via* diffusion in the presence of a concentration gradient between the connected pores. Notional throat diameters are considered in the diffusion modelling to link the size of the diffusing species to throat diffusivity, and to account for sorption effects. A single pore in a cell is shown in Fig. 1c to emphasise that the maximum coordination of a pore in the proposed model is 14. Note, that if S is the size of the cell measured between two square boundaries, the cell volume is $V_c = S^3/2$, and the lengths of the two type of possible throats are: $L_1 = S$ for throats normal to square boundaries; and $L_2 = S\sqrt{3}/2$ for throats normal to hexagonal boundaries.

It is important to remember that the coordination number is not a function of spatial coordinates, but a topological feature of each pore: the number of permeable throats adjacent to the pore. All pores are classified with their coordination numbers to give the coordination spectrum; where the spectrum, in mathematical terms, is a chart describing the structure of the pore space.

The proposed network topology allows for higher pore coordination numbers than models based on cubic lattices [3,4]. Further, the pore coordination spectra that can be generated [5] correspond to published experimental data for macro-porous materials [6,7]. This makes the proposed topology versatile and capable of representing large classes of porous media, with the exception of materials that possess noticeably large fractions of pores coordinated by more than 14 pores. Since there is no experimental evidence for the existence of such materials the model promises to be sufficiently realistic for the purposes of our work.

2.2. Experimental pore size distribution

It is not currently possible to observe the pore connectivity of bentonite directly, like many micro- and meso-porous media, but the distribution of pore sizes can be determined experimentally. We use recently reported data [8], where four different sample preparation techniques have been tested and analysed with a number of experimental techniques to resolve pore size distribution. Of particular interest are the results obtained with high pressure frozen samples which realistically reflect the clay pore space under hydro-geological conditions. The data used in this work is the 3D pore size distribution obtained for hydrated bentonite with focused ion beam nano-tomography. These data are presented as cumulative pore volume *versus* pore radius in [8], revealing total porosity of the sample $\phi = 0.68$. For the construction of the pore network model, the cumulative pore volume against pore radius is converted into the cumulative probability function of pore radii, $F(r)$, using a standard statistical technique, see for example [16].