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Modelling reactive diffusion in clays with two-phase-informed pore networks

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ABSTRACT

Development of pore network models for reactive diffusion of various species in clays is presented. Networks are constructed using experimentally measured pore-space and solid-phase characteristics. This way incomplete experimental information for the topological (pore connectivity) and the geometrical (inter-pore distances) properties of a given pore system can be balanced by known solid-phase properties. Opalinus Clay (OPA) is selected to demonstrate the application and validate the proposed model. OPA is modelled as anisotropic porous medium, reflecting preferential orientation of meso-porosity along clay bedding direction. Bulk diffusivities of various species (HTO, Cl^- and I^-) are calculated to investigate the effects of pore structure, anion exclusion and adsorption. Adsorption is simulated by changing the pore space, which is more realistic compared to existing reactive transport models with assumed constant pore geometry. Anion exclusion effects are simulated by introducing diffuse double layer (DDL) in the model. Results agree well with experimentally measured diffusion coefficients for transport parallel and perpendicular to the bedding direction. The proposed model is applicable to a large class of geo-materials and suitable for linking to lattice models for deformation and damage.

1. Introduction

A thorough understanding of the porous media mass transport is of prime importance in various science and engineering applications, *e.g.*, in radioactive waste disposal (Yu and Neretnieks, 1997; Bourg et al., 2003), in remediation of contaminated groundwater (Grathwohl, 1998), in tracer studies in oil recovery (Whitaker, 1967). The transport properties such as permeability and diffusivity vary with pore space changes due to various mechanical, chemical, physical and thermal processes. These processes can be simulated and analysed by developing appropriate physical and microstructure-informed models. Such models are required to be able to predict measurable transport properties at a macro-scale (considering engineering and geological aspects of the formation) from measurable pore space characteristics such as pore shapes, pore size distribution. Pore-scale level approaches, such as Smoothed Particle Hydrodynamics (SPH) (Zhu and Fox, 2001) and Lattice Boltzmann (LB) (Kang et al., 2006), have been used for computing single and multiphase flow directly on pore-space images. These methods are capable of treating complicated geometries and are very useful for understanding pore morphology effects on transport. However, they are computationally expensive and the conclusions that can be drawn are limited to the imaged pore systems, which are not necessarily representative for a larger volumes of the material analysed. In order to perform simulations on representative elementary volumes (REV) of porous media, such direct methods would require substantial computational effort. Furthermore, pore space information for some materials (such as Opalinus Clay (OPA)) and transport behaviour in these materials is dominated by meso-porosity (pores with diameters between 2 nm and 50 nm) and micro-porosity (pores with diameters smaller than 2 nm) (NAGRA, 2002; Keller et al., 2011). The existing imaging techniques do not have sufficient resolution to obtain detailed 3D images of such materials, to which methods, such as SPH and LB, can be applied.

On the other hand, pore network models (PNM) offer simplicity and computational efficiency that make them very attractive for modelling transport through larger pore structures, *e.g.* of the order of tens to hundreds of inter-pore distances. It should be noted that PNM are conceptually scale indifferent, *i.e.* they can be applied to any length-scale interval where the structure of the pore space has been experimentally observed and analysed. For example, if a particular experimental technique allows for characterising pore features of sizes between 0.1 nm and 50 nm, the corresponding PNM can be constructed to capture effects within this length interval. In addition they provide a suitable representation of mutable pore space structures. In pore network models, the pore space is approximated by a set of sites and a set of bonds connecting some of the sites (Meyers and Liapis, 1999; Dillard and Blunt, 2000). Pore network models have to reflect the basic properties of porous media, such as shape and size distribution of pores and throats, as well as the pore coordination spectrum, *i.e.* the percentages

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of pores coordinated by different number of throats (Gao et al., 2012; Jivkov et al., 2013). These basic properties can be obtained in structures with distinguishable pores and pore throats. However, in materials such as Opalinus Clay (OPA), the pore space is dominated by pores smaller than 50 nm (NAGRA, 2002; Keller et al., 2011), and due to the limitation resolution of current techniques the pore connectivity data cannot be extracted (Jivkov and Xiong, 2014). Hence, for such cases with limited pore space structure information, a different approach is required to construct effective pore networks. Previous approaches to tackle such incomplete pore space information, including predefined connectivity to calculate length scale (Xiong et al., 2014), and variable length scale to calculate connectivity (Jivkov and Xiong, 2014; Xiong and Jivkov, 2015), suffer from lack of an additional constraint. Notably, the length scale refers to the distance between the centres of neighbouring lattice sites, which corresponds to the average inter-pore distances in the porous medium. This can be overcome by considering the solid-phase structure of the material, *e.g.* the shape and size distribution of mineral grains. The solid phase characteristics are incorporated in this work to improve the realism of the constructed pore network model (PNM). The new method developed in the work can be coupled directly to the existing lattice models of the solid-phase previously developed for analysis of damage evolution *via* micro-cracking (Jivkov and Yates, 2012; Zhang and Jivkov, 2014).

The first objective of the work is to develop a methodology of pore network construction for materials with partially available experimental data. The second objective is to develop the model to account for anion exclusion and adsorption effects on the mass transport. The third objective is to validate the method with experimental data, for which OPA is selected.

2. Methodology

2.1. Experimental data

Opalinus Clay displays anisotropic responses to deformation and transport due to preferred orientation (or texture) of clay minerals attained during sedimentation and compaction (Wenk et al., 2008). Specifically, experiments indicated anisotropic diffusion of solute species with slow diffusion perpendicular and fast diffusion parallel to the bedding plane. The goal is to construct a regular PNM in line with available structural data and macroscopic observations.

The pore space used in this work is OPA with sandy facies, labelled BDR in Keller et al. (2011) and Keller et al. (2013a), in which a large number of pores are located predominantly within the fine-grained clay mineral matrix. These pores with sizes >10 nm, called meso-pores, were elongated in the bedding plane, which was resolved by Focused Ion Beam nano-tomography (FIB-nt). The porosity of meso-pores was $\theta_{mes} = 0.018$. Pores with sizes <10 nm, called hereafter micro-pores, occupied approximately 9.7 vol.% (obtained from N_2 adsorption analysis). The porosity of micro-pores is thus $\theta_{mic} = 0.097$. Further, the meso-pores were largely isolated and did not provide a percolating network through the sample. These definitions of micro- and meso-pores are aligned with the commonly used in physical chemistry and may differ from other fields of study.

The above two measurements were combined into a single 'cumulative pore volume fraction — pore radius' curve given in Fig. 1(a) (Keller et al., 2011; Jivkov and Xiong, 2014). For model construction the experimental distribution of Fig. 1(a) is re-evaluated as cumulative probability separately for meso- and micro-pores. These are shown in Fig. 1(b) and Fig. 1(c), respectively.

Regarding the solid phase, Keller et al. (2013b) reported 18 vol.% non-porous carbonates with grain sizes ranging between 100 nm and 300 nm and 17 vol.% of non-porous quartz, the grain size distribution of which was undetermined. For constructing the model for this study, the reported data were converted into cumulative probability of carbonate grain sizes as shown in Fig. 1(d). As both carbonates and quartz are non-porous, the quartz is assumed to follow the size distribution of the carbonate particles due to lack of quartz-specific experimental data.

2.2. Pore network construction

Many pore networks are constructed based on different length scales due to the broad range of pore size distribution. A short overview of existing multi-scale pore network models is presented here.

Jiang et al. (2013) developed a methodology to integrate networks extracted from images at distinct length scales. The pore network model was generated at each scale and then was integrated into a single two-scale network by characterizing the cross-scale connection structure between the two networks. The shortcoming of this method is that it is computationally costly due to the number of network elements (Bultreys et al., 2015). Recognizing the computational problems when single micro-pores are taken into account, Mehmani and Prodanović (2014) proposed a two-scale pore network by packing algorithms. The macro-network is constructed by Delaunay tessellation of the grain centres. Micro-porous networks are generated by downscaling existing networks extracted from macro-pores. This approach was capable of investigating fundamental two-phase flow properties of multi-scale porous media. A clear difference was observed between the behaviour of systems where micro-porosity was able to act in series with the macro-pores (intergranular or pore-filling micro-porosity) and systems where macro-porosity was able to act in parallel the meso-pores (intragranular or dissolution micro-porosity). However, in the construction process, distorted pores were produced when many small grains touched a large grain. In addition, the ratio between macro and micro length scales needs to be determined for micro-porous regions. This ratio is difficult to obtain from image analysis, specifically for clays. Bultreys et al. (2015) developed a workflow to integrate networks of macro-pores and micro-porous regions extracted from micro-CT images. This methodology allowed micro-porosity to act both in parallel and in series with the macro-pore network. However, a representative network for the micro-porosity is necessary. In addition, the pore networks from Jiang et al. (2013)) and Bultreys et al. (2015) are based on experimental data from micro-CT images which did not take into account the micro-pores that cannot be resolved by micro-CT. As the truncated cone shape is used to connect two neighbouring macro-pores, the tortuosity of the connection and geometric details about the bulk of the micro-porous cluster are neglected, which can lead to erroneous local conductivities. In this work, regular networks are used to generate models based on meso-porosity and micro-porosity.

The workflow is as follows: Firstly, the cellular basis is selected for allocation of grains and pores, which results in complementary (dual) lattices for solid and pore systems. In this work, the material was subdivided into cells, in which the truncated octahedrons represented the neighbourhoods of particles in the OPA. The truncated octahedron was the unit cell of a regular space tessellation, proposed for site-bond modelling of solids (Jivkov and Yates, 2012), which was used successfully for mechanical analysis (Jivkov et al., 2012; Zhang and Jivkov, 2014) as well as in the previous works on transport problems (Jivkov et al., 2013; Jivkov and Xiong, 2014; Xiong et al., 2014).

The particles or grains are associated with cell centres (interiors). This is illustrated in Fig. 2(a) for cells with equal distances between the three pairs of square faces, a setup used in previous works (Jivkov and Xiong, 2014; Xiong et al., 2014). The geometry of the cellular assembly is described by three length parameters, S_1, S_2, and S_3, measuring the distances between the square faces in directions (1, 0, 0), (0, 1, 0) and (0, 0, 1), respectively. In an assembly of N_c cells, the particle radius, r_i from Fig. 1(d), is assigned in each cell. The volume of all allocated particles is required to be equal to the experimentally-measured particle volume fraction, ϕ. From this requirement the volume of a cell assembly is