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 geometrical and topological information for 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 sorption. Sorption 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 [1, 2], in remediation of contaminated groundwater [3], in tracer studies in oil recovery [4]. 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 network models (PNMs) provide a suitable representation of mutable pore space structures. In these models, the pore space is approximated by a set of sites and a set of bonds connecting some of the sites [5, 6]. PNMs 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 of pores coordinated by different number of throats [7, 8]. 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 [9, 10], and due to the limitation resolution of current techniques the pore connectivity data cannot be extracted [11]. 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 [12], and variable length scale to calculate connectivity [11], suffer from lack of an additional constraint. 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 PNMs. 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 [13, 14].

The first objective of the work is to develop a methodology for pore network construction for materials with partially available experimental data. The second objective is to develop the model to account for anion exclusion and sorption 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 [15]. Specifically, experiments indicated anisotropic diffusion of solute species with slow diffusion perpendicular and fast diffusion parallel to the bedding plane. Our 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. [9, 16], in which a large number of pores are located predominantly within the fine-grained clay mineral matrix. These pores with radii > 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 N₂ 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.

The above two measurements were combined into a single 'cumulative pore volume fraction – pore radius' curve given in Fig 1(a) [9, 11]. For model construction the experimental distribution from 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. [17] reported 18 vol.% non-porous carbonates with sizes ranging between 100 nm and 300 nm and 17 vol.% of non-porous quartz, the size distribution of which was undetermined. For constructing the model for this study, the reported data was 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.

Fig. 1 Microstructure characteristics of Opalinus Clay: (a) cumulative pore volume fraction versus pore size determined by FIB-nt and N₂ adsorption analyses of sample BDR [9]; (b) cumulative distribution of meso-pore sizes; (c) cumulative distribution of micro-pore sizes with assumed probability density [11]; (d) cumulative distribution of carbonate grain sizes [17].

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. [18] 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 [19]. Recognizing the computational problems when single micro-pores are taken into account, Mehmani and Prodanović [20] 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 and micro-porosity were able to act in series (intergranular or pore-filling micro-porosity) and in parallel (intra-granular or dissolution micro-porosity) to the macro-pores. However, in the construction process, distorted pores produced when many small grains touched a large grain. A parameter, the ratio of the macro to micro length scale, needs to be determined for micro-porous regions from the measurements which may be difficult to obtain. Boultry et al. [19] 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. As the truncated cone shape is used to connect neighbouring two 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, we use regular networks to generate models based on meso-porosity and micro-porosity.

The workflow is as follows: Firstly, we select the cellular basis 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 [13], which was used successfully for mechanical analysis [14, 21] as well as in our previous works on transport problems [8, 11, 12].

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 [11, 12]. 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 calculated by:

$$V_c = \frac{1}{\phi N_c} \sum_{i=1}^{N_c} \frac{4\pi r_i^3}{3} \left(= \frac{1}{2} S_1 S_2 S_3 \right) \quad (1)$$

where V_c is the volume of a cell. The calculation of the three length parameters from Eq. (1) depends on the selection of their ratios used here to represent texture (a non-textured medium would have $S_1 = S_2 = S_3$).

Considering the fact that the reported pore radii are derived with the assumption of cylindrical pore shapes [9], we propose a new pore network structure. Firstly, a skeleton is formed using sites at the centres of cell faces and bonds between neighbouring faces. This is illustrated in Fig. 2(b) on a single cell with $S_1 = S_2 = S_3$. The bonds show the positions where elongated cylindrical pores are allowed to reside, i.e. they represent potential diffusion pathways. Since pores reside on bonds, the sites at face centres represent pore junctions – volume-less containers redirecting mass transport. Then the experimentally measured porosity is mapped to the proposed skeleton. The meso-pores are allocated along cell boundaries according to their size distribution, relative porosity and in preferred direction(s), while the micro-pores with radii selected from Fig. 1(c) are assigned to bonds not already occupied by the meso-pores. The process terminates when the total pore volume fraction attains the experimental porosity. An example of a pore network model assigning meso-pores and micro-pore sets is shown in Fig. 2(c) and Fig. 2(d). More details about meso- and micro-pore allocation can be found in Jivkov and Xiong [11].

Fig. 2 (a) a cellular assembly, illustrating particles of variable sizes allocated to cell interiors; (b) unit cell illustrating potential diffusion paths (bonds) in the neighbourhood of central particle; (c) exclusive assignment of meso-pores along (1, 0, 0) taken as the clay bedding direction; (d) pore network model after assignment of meso-pores (yellow) and micro-pores (red). Examples are given on lattice with equal length parameters for bedding and out-of-bedding directions.

2.3. Pore diffusivities

Real pores and throats have complex and highly irregular geometrical profiles. In this work, a dimensionless circularity G was introduced to approximate throats as cylindrical capillaries with a constant cross section:

$$G = \frac{4\pi A_e}{P^2} \quad (2)$$

where $A_e = \pi R_e^2$ [nm²] is the cross-section area, R_e = radius [nm] and P = perimeter [nm]. The overall pore shape in the clay matrix parallel and perpendicular to the bedding is elongated with a mean circularity of 0.45 [22].

The diffusion in the constructed model is driven by the concentration gradient along the cylindrical pores. For a pore with radius R_e , connecting

nodes n and m , the mass flux of diffusing species, J_e [kg/m²s], is described by the Fick's first law:

$$J_e = -D_p G \Delta C_{nm} / L_e \quad (3)$$

where D_p [m²/s] is the pore diffusivity, L_e [m] is the pore length, and $\Delta C_{nm} = C_n - C_m$ [kg/m³] is the concentration difference between nodes. The pore diffusivity of species of radius r_0 is given by [23]:

$$D_p = D_0 (1 - r_0 / R_e)^4 \quad (4)$$

where D_0 is the free molecular diffusion coefficient of the species in the medium filling the pore system. Pore diffusivities enter a graph-theoretical representation of PNM, allowing for efficient solution of the transport through the network via discrete analysis on graphs as detailed by Jivkov and Xiong [11]. The mass flow through a pore, W , is then $W = J_e \times A_e$.

2.4. Anion exclusion effects

The effective diffusion coefficients, which are a function of the tortuosity and constrictivity in the clay, and the accessible porosity, are different for various solutes [24]. In OPA, diffusion of anions is reduced relative to a neutral tracer such as tritiated water (HTO). The decreased diffusion is explained by anion exclusion effects. The anion exclusion effects are caused by the diffuse double layer (DDL) that surrounds the negatively charged clay surface. To calculate effective diffusion coefficients for anions, e.g. Cl^- and Br^- , the amount of DDL needs to be modelled firstly. As the amount of DDL-water is assumed equal to half of the porosity which is not accessible for anions due to anion exclusion [25], the volume of DDL is achieved by increasing the layer thickness of DDL, r_t , in each pore. If $R_e < r_t$, the anions cannot pass through this pore, otherwise, the anion-accessible pore radius will be $R^* = (R_e - r_t)$.

In this work, we first model the diffusion of HTO to obtain the total porosity, and then, model the Cl^- to find the anion-accessible porosity. The difference gives the amount of DDL-water which is assigned to be devoid of porosity. Iodide has the same accessible porosity as Cl^- . However, the flux front for I^- is retarded compared with that of Cl^- and Br^- . A likely explanation of this retardation is the linear sorption of I^- onto the clay surface [26, 27].

2.5. Sorption effects

OPA has large specific surface area [26], high ion-exchange capacity [26], and sorption affinity for ions, suggesting that long-term diffusivity of such species can be significantly affected by sorption [28]. The amount of species sorbed onto the solid, β , is described by the sorption isotherm, $\beta = \beta(C_M)$,

where C_M is the local concentration of species M in the solution. Different species have linear or nonlinear sorption processes [29].

In order to simulate sorption effect, the sorption of species needs to be judged firstly. In this work, the species are assumed to be strongly adsorbed so that the estimate of the sorption obstruction effect can be obtained by considering the adsorbate to be uniformly smeared into a layer of thickness, t , as described in Xiong et al. [5, 12]:

$$t^2 - 2tR_e + 8\theta R_e r_M / 3 = 0 \quad (5)$$

where r_M is the radius of the diffusing species. If $t < r_M$, the species should be weakly adsorbed. This means that the above sorption equation (Eq. 5) underestimates the sorption obstruction effect [12]. In this case, the sorption effects can be achieved by reducing the radii of throats by a layer of thickness r_M [5]. The radius of a throat after sorption becomes $R^* = R_e - r_M$. The distribution coefficient K_d of Γ is $0.02 \text{ cm}^3/\text{g}$, thus the linear sorption isotherm, β , equals $K_d C_M$ [30].

3. Results and discussion

With respect to a coordinate system (X_1, X_2, X_3) normal to the square faces of the unit cell (see Fig. 2), a pore network skeleton within the boxed region ($0 \leq X_1 \leq 20S_1, 0 \leq X_2 \leq 20S_2, 0 \leq X_3 \leq 20S_3$) was used. The size of the model is sufficiently large to reduce the variation of resulting diffusivity from an average under 10%. The selection of the two boundaries depends on the macroscopic diffusivity being analysed. Specifically, the boundary conditions used to calculate the macroscopic diffusivity D_1 parallel to bedding direction (1, 0, 0) are: prescribed concentration C_0 in all nodes on plane $X_1 = 0$; prescribed concentration C_1 in all nodes on plane $X_1 = 20S_1$; zero flux through all nodes on planes $X_2 = 0, X_2 = 20S_2, X_3 = 0, X_3 = 20S_3$. For calculating the macroscopic diffusivity D_2 perpendicular to the bedding direction, say (0, 1, 0), the boundary conditions are: prescribed concentration C_0 in all nodes on plane $X_2 = 0$; prescribed concentration C_1 in all nodes on plane $X_2 = 20S_2$; zero flux through all nodes on planes $X_1 = 0, X_1 = 20S_1, X_3 = 0, X_3 = 20S_3$.

3.1. Texture effect on diffusivity

The pore networks constructed exhibit macroscopic tortuosity (path lengthening), introduced by the selection of diffusion pathways along the interfaces between solid-phase regions. This tortuosity depends on the material texture, represented here by the ratios of the cell length parameters in three perpendicular directions. Experimental results show that tortuosity is larger in a direction perpendicular to the bedding plane [31]. Therefore,

we investigate the effect of larger cell length along the bedding plane and smaller cell lengths perpendicular to the bedding plane.

The out-of-bedding directions are not differentiated, i.e. the case of having $S_2 = S_3$ is assumed. Three ratios of the cell length parameters are considered: $S_1 / S_2 = 2, 1.5, 1$. For each cellular assembly of given ratio, 10 realisations of pore spatial distributions were analysed to obtain the diffusion coefficients along the bedding plane, D_1 , and out-of-bedding directions, D_2 . The results reported in Fig. 3 are the averaged values of these analyses on the basis of containing 35 vol.% solid particles. The calculated diffusion coefficients of HTO are in the following ranges: $D_1 = 3.09 \times 10^{-11} \sim 5.73 \times 10^{-11} \text{ m}^2/\text{s}$; $D_2 = 1.42 \times 10^{-11} \sim 2.46 \times 10^{-11} \text{ m}^2/\text{s}$ (see Fig. 3). Reported experimentally obtained values for HTO diffusion in OPA shown in Fig. 3 are $D_1 = (5.4 \pm 0.4) \times 10^{-11} \text{ m}^2/\text{s}$ [29, 31] and $D_2 = 1.13 \times 10^{-11} \sim 1.55 \times 10^{-11} \text{ m}^2/\text{s}$ [30, 32]. When $S_1/S_2 = 2$, the simulated results are closest to the experimental values. This ratio is used to calculate diffusivities for anions in the following section. The difference between the computational and the experimental results could be partially due to a difference between the microstructure characteristics of OPA obtained by Keller et al. [9, 16] and used for model construction, and the clays used for experimental measurement of effective diffusion coefficients [30, 32].

Fig. 3. Calculated macroscopic (effective) diffusivity of HTO in OPA. Clay textures are measured by the ratio of length parameters in the bedding, S_1 , and the out-of-bedding, S_2 , directions. D_1 and D_2 are the diffusion coefficients parallel and perpendicular to the bedding plane.

3.2. Anion exclusion and sorption effect on diffusivity

The macroscopic diffusivities of Cl^- and I^- are shown in Table 1. The simulated results of Cl^- are very close to the experimental effective

diffusivities [30]. The predicted D_1 of anions is a little overestimated and D_2 of anions is underestimated. This is in agreement with the expectations for the following reasons. Firstly, allocation of r_t leads to larger number of micro-pores belonging to DDL and a higher increase of macroscopic tortuosity in out-of-bedding directions. Since pores allocated in out-of-bedding directions are only micro-pores and the layer thickness of DDL, r_t , assigned in each pore is the same. A larger fraction of micro-pores is not accessible for the anions in out-of-bedding direction compared to the number of pores in bedding plane direction. As a result, the effective diffusivities in out-of-bedding directions are under estimated. Because the total DDL volume is 50 vol.% of the pores and the micro-pores in out-of-bedding directions contribute more to the DDL volume, the effective diffusivities in the bedding plane direction will be over estimated. Secondly, the accessible porosity for anions should be in a small range [29, 30]. This model can be used to calculate other anion effective diffusivities which only have anion exclusion effects.

The diffusion behaviour of I is the effect of anion exclusion and sorption. Thus, the sorption is simulated on the basis of the same accessible porosity as of Cl . The predicted effective diffusivities of I are in agreement with measured values as shown in Table 1. The over/under estimation of experimental value, D_1 and D_2 , is mainly due to the same reason (exclusion effects) as for Cl . Another reason for difference between predicted results and experimental values could be that the sorption isotherm measured by through-diffusion technique [30] is not quite accurate to describe sorption onto pore walls.

Table1. Comparison of experimental (EXP) and computational (COM) results for diffusion of different species: D_0 =free molecular diffusion coefficient; D_1 = diffusivity in OPA bedding direction; D_2 = diffusivity in OPA out-of-bedding direction. All diffusion coefficients are scaled by $10^{-12} \text{ m}^2/\text{s}$.

Species	D_0	D_1		D_2	
		EXP	MOD	EXP	MOD
Cl	2030	15~17	18	5.31~5.77	3.82
I	2000	10~14	16	4.28~4.86	3.36

Note: The free molecular diffusion coefficients D_0 at room temperature are obtained from Mont Terri Project [29]. Experimental effective diffusivities are obtained from Van Loon, LR [30].

4. Conclusions

This work presented:

- A new method for pore network construction, where solid-phase characteristics of a porous media are used to balance incomplete

- 1 knowledge of geometrical and topological pore system
2 characteristics;
- 3 • A framework for modelling the diffusion anion species due to purely
4 anion exclusion effects in clay. This could be used to clarify the
5 kinds of species transport (anion, cation or neutral species) in OPA,
6 as in most experiments, only species in the source reservoir solution
7 are known. For example, if neutral species with comparable
8 molecular size of HTO are assumed to diffuse in OPA, the
9 accessible porosity applied to HTO could be used to simulate the
10 diffusion of this species. If the simulated effective diffusivities are in
11 good agreement with experimental values, the assumption is correct.
 - 12 • An algorithm to simulate sorption by changing pore space, which is
13 more realistic compared to simulations based on constant pore
14 geometry.
- 15

16 With simulations for three different solutes, it has been demonstrated that
17 the outcomes are within the ranges of reported experimental data,
18 particularly when clay heterogeneity is simulated via different length
19 parameters along bedding plane and in directions perpendicular to the
20 bedding plane. In principle, this model can also be applied to model other
21 neutral species and anions.

22

23 The methodology is particularly suitable for modelling and simulation of
24 micro- and meso-porous materials, such as bentonite and shale rocks. From
25 one side, the existing experimental techniques do not allow for complete
26 quantitative analysis of their pore systems. From another, the effect of
27 damage (micro-cracking) on mass transport in such materials is fundamental
28 to the understanding of their retention or release functions.

29

30 As the description of the network topology is very important for accurately
31 predicting residual phase saturation [33], the feasibility of simulating multi-
32 phase flow by the proposed PNM needs further study.

33

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