PoreFlow: A complex pore-network model for simulation of reactive transport in variably saturated porous media

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A B S T R A C T

This study introduces PoreFlow, a pore-network modeling tool capable of simulating fluid flow and multi-component reactive and adsorptive transport under saturated and variably saturated conditions. PoreFlow includes a variety of modules, such as: pore network generator, drainage simulator, calculation of pressure and velocity distributions, and modeling of reactive solute transport accounting for advection and diffusion. The pore space is represented using a multi-directional pore-network capable of capturing the random structure of a given porous media with user-defined directional connectivities for anisotropic pore structures. The chemical reactions can occur within the liquid phase, as well as between the liquid and solid phases which may result in an evolution of porosity and permeability. Under variably saturated conditions the area of interfaces changes with degree of the fluid saturation.

PoreFlow uses complex formulations for more accurate modeling of transport problems in presence of the nonwetting phase. This is done by refining the discretization within drained pores. An implicit numerical scheme is used to solve the governing equations, and an efficient substitution method is applied to considerably minimize computational times. Several examples are provided, under saturated and variably saturated conditions, to demonstrate the model applicability in hydrogeology problems and petroleum fields. We show that PoreFlow is a powerful tool for upscaling of flow and transport in porous media, utilizing different pore scale information such as various interfaces, phase distributions and local fluxes and concentrations to determine macro scale properties such as average saturation, relative permeability, solute dispersivity, adsorption coefficients, effective diffusion and tortuosity. Such information can be used as constitutive relations within continuum scale governing equations to model physical and chemical processes more accurately at the larger scales.

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1. Introduction

Simulation of variably saturated flow and (multi-component) reactive transport is highly important in many applications involving both natural (soils, rocks, woods, hard and soft tissues, etc.) and industrial (concrete, bioengineered tissues, etc.) porous media. Compared to studies of solute transport at the macro scale, e.g., column scale or field scale (Class et al., 2008; Nick et al., 2011; Geiger et al., 2012), there is less comprehensive research on this subject at the pore scale (Raoof and Hassanizadeh, 2009; Bijeljic et al., 2011; Ovaysi and Piri, 2011). Study of pore-scale processes is essential for explanation and understanding of flow and transport processes at the macro-scale. In addition, pore scale experimental works are often difficult and/or expensive to perform; this makes the use of pore-scale modeling very appealing.

1.1. Issue of scales

Transport in porous media is a multi-scale problem with each scale containing specific information about the underlying physical process (Kechagia et al., 2002; Held and Celia, 2001). The scale hierarchy associated with flow and transport problems in porous media is often divided into: molecular scale, micro or pore scale, macro or lab scale, meso or field scale, and mega or regional scale. While modeling at a larger scale, it is usually not feasible to take all pore-scale properties, such as interfaces, into account. However, their lumped effects must be included in macro-scale descriptions (Raoof et al., 2010). Since pore-scale modeling provides a bridge between pore scale and macro scale representation of processes, it is a useful tool to study averaging effects, to explore how pore scale processes manifest themselves in macroscopic level (core or field scale). Pore-scale models can be used to elucidate the pore-scale nature of processes such as: spreading of solute due to deviations in pore velocities, adsorption of solutes or colloids to the grain surfaces under saturated conditions,
reaction at the nonwetting–wetting interfaces under variably saturated conditions.

1.2. Pore-network modeling applications

Modeling fluid flow in porous media at the macro-scale requires specification of the constitutive properties of the porous medium. Examples are: (i) the relationship between the capillary pressure, $P_c$ (the difference between the pressures of the nonwetting and wetting fluids) and the fluid saturation, $S_w$, (ii) the relative permeability, $k_r$, as a function of either the saturation or capillary pressure, and (iii) the relationship between solute dispersivity or effective diffusion and saturation in solute transport processes.

The relative permeability of a fluid is a measure of the conductance of the porous medium for that fluid at a given saturation. Relative permeability measurements on field samples are difficult and time consuming. In general, experimental determination of the $P_c–S_w$ relationship is easier than measurement of relative permeability. For this reason, empirical relationships, such as those of Brooks and Corey (1964) and Van Genuchten (1980), are often used to model the dependence of relative permeability on capillary pressure or saturation (e.g., Nick and Matthaëi, 2011).

As another approach, one may use pore network models (PNMs) to obtain constitutive properties. One of the early attempts to estimate relative permeability was to use bundle-of-capillary-tubes models. This was based on the assumption that a porous medium may be modeled as bundle of capillary tubes of various diameters. However, such models ignore the interconnected nature of porous media and often do not provide realistic results. PNMs, first suggested by Fatt (1956), offer a more realistic approach for calculating constitutive properties. The vast majority of PNMs consist of pore bodies (or nodes) and pore throats (or channels), along with a specified topological configuration which prescribes how pore bodies are connected via pore throats. Pore bodies are meant to represent larger void spaces found in natural porous media. The narrow openings that connect adjacent pore bodies are modeled by pore throats, which are essentially capillary tubes. The pore-network approach for modeling multiphase flow properties has been extensively employed in the petroleum engineering literature (Chatzis and Dullien, 1985; Celia et al., 1995; Blunt, 2001; Algive et al., 2012). In recent years, various pore network models have been developed to explore chemical and biological processes, such as: dissolution of organic liquids (Zhou et al., 2000; Held and Celia, 2001; Knutson et al., 2001); CO$_2$ sequestration (Kang et al., 2010; Kim et al., 2011; Mehrani et al., 2012; Raoof et al., 2012; Varloteaux et al., 2013); biomass growth (Suchomel et al., 1998a; Kim and Fogler, 2000; Dupin et al., 2001; Gharasoo et al., 2012; Rosenzweig et al., 2013); solute dispersivity (Vasilyev et al., 2012), and adsorption (Acharya et al., 2005; Li et al., 2006; Raoof et al., 2010; Köhne et al., 2011).

Because of their ability to simulate the highly disordered geometry of pore space and relatively low computational cost (e.g., in comparison with Lattice Boltzmann simulation, Sholokhova et al., 2009), PNMs hold promise as tools for predicting multiphase flow properties of specific porous media. For example, the dependence of capillary pressure on saturation is modeled by determining the location of fluid–fluid interfaces throughout the network using the Young–Laplace equation. This is sometimes modified by other pore-level mechanisms, such as snapoff during imbibition (e.g., Yu and Wardlaw, 1986). Also, the dependence of relative permeability on saturation is determined by computing the resistance to flow in the connected portion of a fluid. In these calculations, resistance to the flow within the pore bodies is commonly ignored, assuming that conductance within the pore bodies is much larger than the conductance within the pore throats. Commonly, an average pressure and/or concentration is assigned to a given pore body or pore throat. For each pore, change in solute mass is described by mass balance equations (Lichtner, 1985). Using information on local surface area, and applying an area-normalized reaction rate, a kinetic reaction is calculated for each pore (Raoof et al., 2010).

One shortcoming of a pore-network model is its idealization of the pore space using simple geometries; often, pores are assumed to have uniform circular or square cross-sectional shapes. This makes it difficult to simulate some processes, such as biogeochemical reactions, that could lead to a significant change in complex pore geometries as a result of dissolution, precipitation, and/or biological clogging. However, pore-network models are computationally cheap, and recent advances have allowed modeling a degree of irregularity in channel cross-sectional shapes. In addition, pore-network models are capable of capturing important statistical characteristics of porous media such as pore size distributions (Oren et al., 1998; Lindquist et al., 2000), together with coordination number distributions (Raoof and Hassanizadeh, 2009) and topological parameters such as Euler number (Vogel and Roth, 2001).

1.3. Objective

The objective of this article is to introduce a simulation tool, called PoreFlow, for simulation of pore-scale flow and reactive/adsorptive transport in two- and three-dimensional domains. PoreFlow has several features which makes it a powerful tool for pore-scale modeling. It allows us to model several different processes, starting from generation of a pore network model for a specific porous media up to the simulation of drainage and (two-phase) fluid flow and reactive/adsorptive solute or colloid transport (with possible changes in pore sizes), under both saturated and variably saturated conditions. In addition, PoreFlow assigns volumes to both pore bodies and pore throats and, unlike other pore network simulators, it refines discretization of drained pores to simulate flow and transport more accurately in the presence of the nonwetting phase. Doing so, we can calculate velocity and concentration distributions within drained pores. Using such a model, one can obtain different pore-scale information for a given porous structure and derive various constitutive relations to be used within macro-scale models appropriate for modeling at the continuum scale.

We start with a brief description of the software structure, followed by an explanation of the model features. This includes a presentation of the governing equations, and their discretization in space and time. Then, several examples are used to illustrate applicability of this code under various flow and transport conditions.

2. PoreFlow structure and methods

In this section, we present the structure of the modeling tool, simulation modes, and the coupling between different processes.

2.1. Coupled model

PoreFlow uses a Multi-Directional Pore-Network (MDPN) to represent porous media, and performs flow and solute transport simulations in such a network. The numerical scheme is developed based on the assumption that porous medium can be represented as a network of pore bodies and pore throats, both with finite volumes. There are two options to simulate the transport part: (i) advection only and (ii) advection and diffusion. When including multicomponent chemical reactions, Biogeochemical Reaction Network Simulator (BRNS) (Regnier et al., 2002) performs the
adsorption/reaction part. This gives major advantages for simulation of complex reaction systems.

In the case of chemical reactions with the solid surface (for example, dissolution/precipitation processes), the pore sizes will change, which in turn will cause changes in porosity and permeability. In such cases, after each reaction time step the flow field is updated. In the discretized time domain, the solute transport and reaction processes are solved using a non-iterative sequential split operator approach. The model benefits from an adaptive time stepping approach for geochemical computations within the iterative schemes.

A summary of computational features of PoreFlow is as follows:

- The topology of the pore space is modeled using a Multi-Directional Pore Network (MDPN) which allows a distribution of coordination numbers ranging between 1 and 26.
- To take into account the angularity of pores in natural porous media, pore throats are assigned a variety of cross sectional shapes, with a wide range of shape factors. This includes rectangular, circular, and various irregular triangular cross sections.
- Both pore bodies and pore throats have volumes. This means we solve mass balance equations and calculate solute concentrations and mass fluxes within both pore bodies and pore throats.
- The pore body sizes can be taken from various statistical distributions. The pore-throat sizes can be either correlated to the pore body size distribution or chosen to be independent from pore body sizes.
- A drained pore body is refined into smaller compartments occupied by the wetting phase, each with its own concentration. This takes into account the effect of limited mixing due to the partial filling of a drained pore body by the nonwetting phase.
- Upon invasion of an angular pore throat by the nonwetting phase, each edge of the pore throat will be considered as a separate domain with its own flow rate and concentration.
- Fully implicit numerical schemes are employed for calculating solute concentrations at each time step. Efficient substitution method is applied which considerably reduces the computational time.
- BRNS is used for simulating various multicomponent geochemical and microbiological processes.
- Various parameters and relations, such as coefficient of variation of pore velocities, capillary pressure–saturation (Pc–Sw) curves, relative permeability–saturation curves, interfacial area, solute dispersivity–saturation relation, effective diffusion, tortuosity, and the fraction of percolating saturated pores are also computed.

Fig. 1 shows the flowchart of PoreFlow. Besides the capability of PoreFlow to generate Multi-Directional Pore Networks, it is possible to generate pore networks with regular patterns as well as user-defined pore connections (Raoof, 2011). The structure of the network can be optimized (using a Genetic Algorithm routine Raoof and Hassanizadeh, 2009) in order to obtain a pore network with a specific coordination number distribution. During the simulation, the data are transferred to MATLAB, using MATLAB Engine functions, for the purpose of analysis and postprocessing.

2.2. Pore-network modeling

In this section we introduce properties of the pore network following by discretization method used within PoreFlow.

2.2.1. Coordination number distribution in MDPN

A pore body coordination number, z, is defined as the number of pore throats connected to it. Most pore-network models have a regular network with a fixed coordination number of six for all pore bodies (except those at the boundaries). This means that any given pore body is connected to six neighboring nodes via tubes that are oriented along the lattice axes in three principal directions (directions number 1, 2, and 3 in Fig. 2). However, there is overwhelming evidence that a very wide range of coordination numbers exists in a real porous medium (Jimkov et al., 2013). For example, Ioannidis et al. (1997) determined the mean coordination number, Z, from serial sections of a sandstone core, and found it to be 3.5. Oren and coworkers (Oren et al., 1998; Oren and Bakke, 2003) developed a process-based reconstruction procedure, which incorporated grain size distribution and other petrographical data obtained from 2D thin sections. They reported mean coordination numbers of 3.5–4.5 (Oren and Bakke, 2003).

One of the main features of MDPN is that pore throats can be oriented in 13 different directions, allowing a maximum coordination number of 26, as shown in Fig. 2. Then, to get a desired coordination number distribution, we follow an elimination procedure to rule out some of the connections. The elimination procedure is such that a pre-specified mean coordination number can be obtained. A coordination number of zero means that the pore body is eliminated from the network, so there is no pore body located at that lattice point. Pore bodies with the coordination number of one could be eliminated when dead end pores are not considered, except if they are located at the inlet or outlet boundaries (so they belong to the flowing fluid backbone). This network generation method was successfully employed to develop networks that very closely modeled real sandstone as well as granular media, using information on their coordination number distributions. The detail of the network generation method can be found in Raoof and Hassanizadeh (2009). The distribution of coordination number and a representative domain of the network used in this study are given in Fig. 3.

2.2.2. Determination of the pore cross section and corner half angles

A key characteristic of real porous media is the angular form of pores. It has been demonstrated that having pores with a circular cross section, and thus single-phase occupancy, causes insufficient connectivity of the wetting phase and as a result poor representation of experimental data (Zhou et al., 2000). Angular cross sections retain the wetting fluid in their corner and allow two or more fluids to flow simultaneously through the same pore. Pores which are angular in cross section are thus a much more realistic model than the commonly employed cylindrical shape. In PoreFlow, different pore throats are assigned a variety of cross sectional shapes including circular, rectangular, and scalene triangular.

The shape of an angular pore cross section is prescribed in terms of a dimensionless shape factor, G (Mason and Morrow, 1991), which is defined as

\[
G = \frac{A}{P^2}.
\]

where A and P are the area and the perimeter of the cross section, respectively. The shape factor replaces the irregular and complicated shape of a pore throat by an equivalent either circle, triangle, or rectangle shape. The value of shape factors ranges from a minimum of zero corresponding to a slit to a maximum of 0.08 corresponding to a circular cross section. Values of shape factors for triangular cross sections vary from 0 to 0.048 (with maximum for equilateral triangle), and rectangular cross section from 0 to 0.062 (with maximum for square shape).
2.2.3. *Pore space discretization*

PoreFlow uses a new approach to discretizing the pore space for calculation of the fluid flows and solute concentrations. The continuous pore space is discretized into "pore elements", each with its own pressure, concentration, and adsorbed mass, etc. The discretization depends on saturation state of a pore as follows.

In the case of a saturated pore, one pressure and one concentration values are assigned for each pore element representing either a saturated pore body or a pore throat. In the presence of the nonwetting phase, a given pore body or pore throat could be invaded and partially filled by the nonwetting phase, forcing the wetting phase to flow only along the edges. Fig. 4a shows a schematic example of two pore bodies connected to each other using a pore throat with an angular cross section. Under such conditions, pore throats are not necessarily the narrowest constriction along the flow path, anymore. In fact, resistance to the flow within the edges of drained pore bodies may be comparable to, or even larger than, the resistance to the flow within the pore.
of them being a pore element. As shown in Fig 4a, a corner unit is composed of a corner together with half pore body edges connected to it. For example, a cubic pore body consists of 8 different pore elements with 8 different pressure and concentration values assigned to them. Fluid flow and solute mass fluxes between these elements occurs through 12 edges within drained pore body.

In a drained pore throat with angular cross section, there will be flow of wetting phase only through the edges of the pore throats. Since in an angular pore edges may have different angles, they have different flow rates, and presence of the nonwetting phase limits mixing between them. To take this effect into account, each edge of a drained pore throat is treated as a pore element with its own flow rate and concentration value.

The conductance of each edge within drained pore bodies or pore throats needs to be determined as a function of the thickness of the wetting film residing in the edge. This thickness depends on the radius of curvature of the fluid–fluid interface, which in turn depends on the capillary pressure. Corner units of a given drained pore body are connected to the neighboring pore body corners via pore throats. This means that we need to specify connections of pore throats to the corners of pore bodies, which is done through a random process. The detail of algorithm which has been used to associate different pore throats to different corners of neighboring pore bodies can be found in Raoof and Hassanizadeh (2012).

### 2.3. Variably saturated flow modeling

To simulate a drainage process, the nonwetting phase is considered to enter the network through an external reservoir which is connected to the inlet side of the network. The displaced phase escapes through the outlet face on the opposite side.

#### 2.3.1. Drainage simulation

At low flow rates, the progress of the displacement is controlled by capillary forces. This forms the basis for the invasion–percolation algorithm (Wilkinson and Willemsen, 1983; Chandler et al., 1982) used to model drainage in PoreFlow. At every stage of the process, nonwetting phase invades all accessible pore bodies and throats with the lowest entry capillary pressure. The entry capillary pressure is given by Laplace equation (Bear, 1988),

$$\frac{P_n - P_w}{\gamma_{\text{wn}}} = \frac{1}{r_1} + \frac{1}{r_2} = \frac{2\gamma_{\text{wn}}}{r^*},$$

where $P_w$ and $P_n$ are the pressure of the wetting and the nonwetting phases, respectively, $r^*$ is the mean radius of curvature and $\gamma_{\text{wn}}$ is the surface tension. For a capillary tube of radius $r$, we have $r^* = r/\cos(\theta)$ (Young–Laplace’s equation), in which $\theta$ is the contact angle between fluid interface and capillary wall. The invading fluid enters and fills an available pore throat only when the injection pressure is equal to or larger than the entry capillary pressure of the pore.

The wetting phase is hydraulically connected through filaments within edges of angular pores. The capillary pressure is increased incrementally so that fluid–fluid interfaces will move only a short distance before coming to rest in equilibrium at the opening of slightly smaller pore throats.

#### 2.3.2. Fluid flow within drained pores

After performing the drainage step, knowing the curvature of interfaces and local saturations in each pore, PoreFlow calculates conductances of edges of the drained pores throats and drained pore bodies as well as conductances of saturated pores. Conductances are needed to calculate the flow across the network, which is due to the flow of wetting phase in saturated pores as well as along edges of drained pore bodies and pore throats. The conductance of an angular drained pore depends on its degree of local

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**Fig. 2.** Schematic of a network consisting of three pore bodies in each direction (i.e., $N_1=3$, $N_2=3$, $N_k=3$). Numbers inside squares denote all possible throat directions and plain numbers are pore body numbers. To keep the figure less crowded, only throats which are connecting pore body 14 to its neighboring pore bodies are shown [After, Raoof and Hassanizadeh, 2009].

**Fig. 3.** The coordination number distribution and a representative domain of Multi-Directional Pore-Network (MDPN).
saturation, which is directly related to the radius of curvature of the meniscus formed along the pore edges. Raoof and Hassanizadeh (2012) used a numerical solutions to calculate the dimensionless conductances of drained pores with angular cross section. This was done by numerically solving the dimensionless form of the Navier–Stokes equations and the equation of conservation of mass. Through this method, knowing the geometry of the pore, one can calculate the conductance of a given edge of a pore body or pore throat.

3. Simulating flow and transport within the network

3.1. Flow simulation

The flow field is established in the network by imposing a pressure difference across the network. All other boundaries of the network parallel to the overall flow direction are treated as no-flow boundaries. We assume that the discharge through a given drained pore throat can be prescribed by Hagen–Poiseuille equation:

$$q_{ij} = \sum_{k=1}^{N_{edg}} \left( \frac{p_j - p_l}{R_{ij,k}} \right),$$

(3)

where $q_{ij}$ is the total volumetric flow rate through pore throat $ij$, $R_{ij,k}$ is conductance of kth edge of angular pore throat $ij$, and $p_l$ and $p_j$ are pressures at pore elements $i$ and $j$, respectively. Eq. (3) is valid for laminar flow in a wide range of Reynolds numbers and is assumed to be appropriate for describing flow in pores (Bear, 1972).

For incompressible, steady-state flow, the sum of discharges into and out of a pore body, or a pore-body corner unit in the case of a drained pore body, must be zero. For the pore bodies, the continuity equation may be written as

$$\sum_{n=1}^{N_{edg}} q_{in} + \sum_{j=1}^{z_i} q_{ij,\text{tot}} = 0; \quad j = 1, 2, \ldots, z_i,$$

(4)

where $N_{edg}^{CU}$ shows the number of edges through which corner unit $i$, within a drained pore body, is connected to other corner units, $n$, within the same pore body, $z_i$ is the coordination number of pore $i$. Eq. (4) is applied to all pore bodies except those on the two flow boundaries where pressures are specified. Combination of Eqs. (3) and (4) for all pores results in a linear system of equations, with a sparse, symmetric and positive-definite coefficient matrix, to be solved for pore body pressures. Then, the flow velocity in all pore throats can be calculated using Eq. (3).

Considering the network as an REV, the average pore velocity $\nabla$ can be determined as

$$\nabla = \frac{Q_{tot} L}{V_f},$$

(5)

where $Q_{tot}$ is the total discharge through the network which is the sum of fluxes through all pore throats at the inlet or outlet boundary of the network, $L$ is the network length, and $V_f$ is total fluid volume.

Knowing the total discharge through the network, we can also calculate the relative permeability. The relative permeability of the network to the wetting phase at a given saturation and capillary pressure is calculated using Darcy’s law,

$$k_{nw} = \frac{\mu \cdot Q_{tot}}{k A \Delta P / L},$$

(6)

where $\mu$ is the viscosity, $k$ is the intrinsic permeability, and $\Delta P$ is the pressure difference between inflow and outflow reservoirs. Repetition of this process at consecutively larger imposed capillary pressures results in a graph of capillary pressure versus saturation and relative permeability versus saturation.

3.2. Adsorptive solute/colloids transport, without diffusion

As mentioned earlier, we assume that the solutes or colloids maybe adsorbed to the fluid-fluid (i.e., nonwetting–wetting) interfaces (shown by NW) in drained pores as well as to solid–fluid (i.e., solid–wetting) interfaces (shown by SW). Based on the definition of pore element given in Section 2.2.3, the unknowns to be solved for are either concentrations of saturated pore bodies, $c_i$, and saturated pore throats, $c_{ip}$ or concentrations of edges of drained pore throats, $c_{ij,k}$, and corner units of drained pore bodies, $c_{CU,j}$. The adsorbed mass concentrations in the case of saturated pores will be the adsorbed mass concentrations of saturated pore bodies, $s_{mix}$, and saturated pore throats, $s_{ij,mix}$. In the case of variably saturated pores, they will be adsorbed mass concentrations at SW and NW interfaces of drained pore throats, $s_{ij,k}^{SW}$ and, $s_{ij,k}^{NW}$, respectively, and adsorbed to interfaces of corner units of drained pore bodies, $s_{i,j}^{CU}$ and, $s_{i,j}^{CU}$, respectively.

To present the formulation, we provide the mass balance equations for a pore body corner unit $i$ and a drained angular pore throat, similar to those shown in Fig. 4a. Indeed, the mass balance equations should be written for a given chemical component $l$, with the concentration of $c_l$. However, to keep the equations less crowded we drop the superscript $l$ from the concentrations throughout this manuscript. We assume that the flow is from corner unit $j$ toward corner unit $i$ through corners of drained pore throat $ij$. For a given corner unit (with concentration $c_{CU,j}$ and

![Fig. 4](image-url)
volume $V_{CU}$, we can write the following mass balance equation:

$$
\frac{d}{dt} C_{CU} = \sum_{j=1}^{N_{tube}} \sum_{k} \frac{N_{ij}^{sw}}{V_{ij}} \left( c_{ij} - q_{ij,k} c_{ijk} - \frac{N_{ij}^{sw}}{V_{ij}} \right) - \frac{N_{ij}^{sw}}{V_{ij}} C_{CU},
$$

where the first term on the r.h.s. is due to the mass influx via $N_{ij}^{sw}$ edges of $N_{in}$ throat throats with flow toward the corner unit $i$. The second term on the r.h.s. accounts for the mass influx from $N_{ij}^{sw}$ neighboring corner units (within the same pore body) with flow toward corner unit $i$. The third term shows the mass leaving the corner unit, where $Q_{CU}$ is the total flux leaving (or entering) the corner unit $i$. The last two terms account for the mass adsorbed onto the solid walls of the corner unit and on the NW interface within the corner unit, respectively. $s_{ij}^{sw}$ [ML$^{-3}$] and $s_{ij}^{nw}$ are the mass adsorbed to SW and NW interfaces per unit volume of the corner unit.

We should note that, in the case of saturated pores, the second term on the right-hand-side of Eq. (7) vanishes, and the value of $N_{ij}^{nw}$ in the first term will be equal to one, since there is no edge flow present.

To close the system, we need extra equations for $s_{ij}^{sw}$ and $s_{ij}^{nw}$. Here, we assume linear equilibrium adsorption at both SW and NW interfaces, such that

$$
\begin{align*}
\bar{s}_{ij}^{sw} &= k_{ij}^{sw} q_{ij,k} c_{ijk}, \\
\bar{s}_{ij}^{nw} &= k_{ij}^{nw} q_{ij,k} c_{ijk},
\end{align*}
$$

where $k_{ij}^{sw}$ and $k_{ij}^{nw}$ [L] are pore scale adsorption distribution coefficients at SW and NW interfaces, respectively. The specific surface area, $a_{ij}^{sw}$, is defined as

$$
a_{ij}^{sw} = \frac{\bar{s}_{ij}^{sw}}{V_{ij}}.
$$

Within the pore throats we assume linear equilibrium adsorption, so that we can write

$$
\begin{align*}
\bar{s}_{ij,k}^{sw} &= k_{ij,k}^{sw} a_{ij,k} q_{ij,k}, \\
\bar{s}_{ij,k}^{nw} &= k_{ij,k}^{nw} a_{ij,k} q_{ij,k},
\end{align*}
$$

where $k_{ij,k}^{sw}$ and $k_{ij,k}^{nw}$ [L] are pore scale adsorption distribution coefficients at SW and NW interfaces, respectively. The specific surface area, $a_{ij,k}^{sw}$, is defined as

$$
a_{ij,k}^{sw} = \frac{\bar{s}_{ij,k}^{sw}}{V_{ij,k}}.
$$

Combining Eqs. (7) through (12) results in a linear set of equations to be solved for $c_{ijk}$ and $C_{CU}$. Since we discretize pore bodies and pore throats on the basis of their saturation state (i.e., depending on whether a pore is saturated or invaded by the nonwetting phase), the number of unknowns depends on saturation. In the case of a fully saturated domain, the number of unknowns is equal to $N_{tube} + N_{node}$ ($N_{tube}$ is the total number of pore throats and $N_{node}$ is the total number of pore bodies). In general, the number of pore throats is larger than the number of pore bodies in pore network models. In order to increase numerical efficiency, first, applying a fully implicit scheme, we discretize Eq. (10) and determine $c_{ijkl}$ in terms of $C_{CU}$. This is then substituted into the discretized form of Eq. (7), resulting in a set of equations for $C_{CU}$ (Raoof et al., 2010). This method considerably reduces the computational times. For the accuracy of the scheme, the minimum time step is chosen on the basis of residence times (Suchomel et al., 1998),

$$
\Delta t \leq \min(T_{ij}, T_{ik}, T_{CU}, T_{ij}).
$$

where $T$ denotes the residence time pertaining to different elements within the pore network. It is the volume of the element filled by the wetting phase divided by the flux of wetting phase through the element.

After obtaining the solution at each time step, breakthrough curves (BTCs) at a given longitudinal position are calculated by averaging the concentrations of pore bodies centered at that position. In calculating BTCs, the concentrations of pore bodies are weighted by their volumetric flow rate, resulting in a flux-averaged concentration. That is, the normalized average concentration, $\tau(x,t)$, given by

$$
\tau(x,t) = \frac{\sum_{i=1}^{N_{node}} c_{i}(x,t) Q_{i}}{\sum_{i=1}^{N_{node}} Q_{i}},
$$

where $c_{i}$ is inlet solute concentration and $N_{node}$ denotes the total number of pore body elements that are located at the longitudinal coordinate $x$. The longitudinal coordinate can be written as multiples of lattice size $\epsilon$, i.e., $x = 1/\epsilon, 2/\epsilon, ..., L$, where $\epsilon$ is the horizontal distance between centers of two adjacent pore bodies. The breakthrough curve at the outlet is obtained by plotting $\tau(x,L,t)$.

3.3. Solute transport, including diffusion

For the case of reactive solute transport through the network including both advection and diffusion, the mass balance Eq. (7) for a pore body corner unit is extended to the following form:

$$
\frac{d}{dt} C_{CU} = \sum_{j=1}^{N_{tube}} \sum_{k} \frac{N_{ij}^{sw}}{V_{ij}} \left( c_{ij} - q_{ij,k} c_{ijk} - \frac{N_{ij}^{sw}}{V_{ij}} \right) - \frac{N_{ij}^{sw}}{V_{ij}} C_{CU},
$$

where $N_{ij}^{sw}$ are the concentrations of masses adsorbed at SW and NW interfaces, respectively.

The fourth and fifth terms show the diffusive mass flux between corner unit $i$ and $N_{ij}^{nw}$ pore throats as well as $N_{ij}^{nw}$ corner units connected to it. $D$ is the molecular diffusion coefficient and $A_{ij}$ is the cross section of $k$th edge of tube $i$, which is a function of saturation. $A_{in}$ is the cross section of the pore body edge connecting corner unit $i$ to corner unit $n$. We should note that, for the case of saturated pores, there is no edge flow present and the value of $N_{ij}^{nw}$ will be equal to one.

Similarly, the mass balance Eq. (10) for an edge element of a drained pore throat (assuming that corner unit $j$ is the upstream node) is modified to

$$
\frac{d}{dt} C_{ij} = |q_{ij,k}| c_{ij,k} - |q_{ij,k}| c_{ijk} + DA_{ij} \left( C_{ij} - C_{ij,k} \right)/l_{ij} + DA_{ij} \left( C_{ij,n} - C_{ij,k} \right)/l_{ij} - R_{ij},
$$

In Eqs. (15) and (16), $R_{ij}$ and $R_{ik}$ represent the reaction terms for corner units of drained pore body $i$ and $k$th edge of drained pore throat $ij$, respectively. Note that for multi-component transport...
these parameters should be rewritten as $K_i \rho_i$ and $K_{eq}$ for each chemical species $i$.

### 3.4. Biogeochemical Reaction Network Simulator (BRNS)

PoreFlow uses Biogeochemical Reaction Network Simulator (BRNS) (Regnier et al., 2002) for solving a set of coupled nonlinear equations modeling reactive solutes. BRNS has been used as a flexible numerical engine applicable for a variety of reactive transport problems in surface and sub-surface environments such as, groundwater contamination, interaction between groundwater and sea water, seafloor carbon burial, and enhanced oil recovery (Jourabchi et al., 2005; Sipeti et al., 2006b; Thullner et al., 2008; Nick et al., 2013). One of the main features of BRNS is an automated procedure for code generation using a MAPLE interface. This provides high flexibility to include and combine alternative biogeochemical process descriptions in the model. Using this interface, kinetically controlled and equilibrium reactions, and combinations of both can be specified with arbitrary form of equations describing the transformations of the chemical species. A description on how symbolic programming can be used to create the model specific source code necessary to the numerical solution of the governing equations is explained in Regnier et al. (2002).

The reactive processes, rate parameters and equilibrium constants, species involved, and stoichiometry are required to define a specific reaction network and to solve for the reactive terms in each pore body and pore throats (i.e., reaction terms in Eqs. (15) and (16)). The reaction term representing the sum of reactions affecting concentration of a given species $i$ can be written as

$$ R_i = \sum_{m=1}^{N_{reaction}} \theta_i^{m} m_i, $$

where $N_{reaction}$ is the number of reactions, $\theta_i^m$ represents, for kinetic reactions, the rate of the reaction $m$ and $m_i$ is the stoichiometric coefficient of species $i$ in the reaction $m$. The form of rate expression, $\theta_i^m$, is arbitrary, even nonlinear, and can be a function of several concentrations within the system.

The MAPLE interface is employed to generate Fortran files, such as the function residuals, which represent the reaction network, and the Jacobian matrix, which contains the partial derivatives of the function residuals with respect to the unknown concentrations. The generated Fortran files and the solver engine for solving a nonlinear set of equations ensued from kinetic and equilibrium reactions of multi components are embedded in PoreFlow. The reactive solver uses a Newton–Raphson method to linearize the set of kinetic and equilibrium reaction equations. In this work a sequential non-iterative approach is implemented. Within the employed sequential approach, first the transport step, and then the reactive step is solved in each time step of the simulation.

### 4. Application examples

In this section, we present results for various simulations of (variably) saturated flow and (reactive/adsorptive) transport using PoreFlow.

#### 4.1. Non-reactive transport; saturated conditions

As the first example, we present results obtained using PoreFlow to simulate transport of a tracer solute through a column. We consider the case of a pulse input of the solute. Averaging over the network cross section results in a 1D concentration field. At the macro-scale, solute transport through a column is modeled by the Advection Dispersion Equation (ADE),

$${\partial \over \partial t} \rho \phi \xi + \phi {\partial \rho \phi \xi \over \partial x} = \phi D_l \partial^2 \rho \phi \xi \over \partial x^2,$$

where $\phi$ is porosity, $\xi$ is average pore velocity, and $D_l$ is the longitudinal dispersion coefficient. In this equation, porosity and $\xi$ values are determined directly from the pore network and $D_l$ is estimated by fitting Eq. (18) to the breakthrough curves calculated using PNM.

To verify the pore network model, we compare the resulting breakthrough curve from the pore network model with the analytical solution of Eq. (18) representing the macro-scale behavior for the same value of porosity, average velocity, and the domain length as in the pore network. We use a network of size $N_i = 40, N_j = N_k = 20$ (Model 1) with an average velocity of 0.72 m/d. The properties of the generated network are given in Table 1. A pulse tracer concentration of one is injected through the inlet boundary for 1.8 pore volumes. At various time steps concentrations at the outlet face of the network are averaged over the cross section to obtain the breakthrough curve. Fig. 5 shows the resulting BTC together with the analytical solution. The agreement with the analytical solution shows the accuracy of the numerical scheme.

#### 4.2. Non-reactive transport; variably saturated conditions

An important parameter under variably saturated conditions is solute dispersion coefficient, that depends not only on the Darcy velocity but also on degree of saturation, which has been shown by

<table>
<thead>
<tr>
<th>Characteristic</th>
<th>Model 1</th>
<th>Model 2</th>
<th>Model 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial $N_{node}$ (before elimination)</td>
<td>1,875</td>
<td>3,363</td>
<td>9,792</td>
</tr>
<tr>
<td>Initial $N_{node}$ (before elimination)</td>
<td>16,000</td>
<td>30,000</td>
<td>10,000</td>
</tr>
<tr>
<td>$N_{node}$ (after elimination)</td>
<td>33,239</td>
<td>86,888</td>
<td>29,31</td>
</tr>
<tr>
<td>$N_{node}$ (after elimination)</td>
<td>14,804</td>
<td>29,257</td>
<td>977</td>
</tr>
<tr>
<td>Connections to the inlet boundary</td>
<td>578</td>
<td>215</td>
<td>237</td>
</tr>
<tr>
<td>Connections to the outlet boundary</td>
<td>581</td>
<td>193</td>
<td>265</td>
</tr>
<tr>
<td>Pore bodies on the inlet boundary</td>
<td>315</td>
<td>91</td>
<td>93</td>
</tr>
<tr>
<td>Pore bodies on the outlet boundary</td>
<td>313</td>
<td>86</td>
<td>92</td>
</tr>
<tr>
<td>Porosity</td>
<td>0.25</td>
<td>0.27</td>
<td>0.12</td>
</tr>
</tbody>
</table>

![Fig. 5. Comparison of BTC obtained from pore network (Model 1) with analytical solution for a pulse input of solute to a column. The solid line shows average concentration at the outlet of the network and the symbols are analytical solution of continuum scale Eq. (18).](image-url)
Raoof and Hassanizadeh (2013) through pore scale modeling and comparison with experimental data reported by Toride et al. (2003).

The degree of spreading of solutes is related to distribution of the pore velocities within the pore spaces. Decrease in saturation creates corner flows within drained pores and increases pore velocity fluctuations, which results in a higher solute dispersion coefficient (Toride et al., 2003). Using PoreFlow, we can simulate transport of solutes under different saturation levels (Raoof and Hassanizadeh, 2013). Since, resistance to the flow is included within drained pore bodies and pore throats, different fluxes are calculated for different edges of each drained pore, which are used in the calculation of solute transport. Fig. 6 shows the BTCs of tracer solute obtained under three different saturations for Model 1. There is a greater spreading of solute (i.e., higher dispersivity) under lower saturations due to the presence of longer flow paths, and wider distribution of arrival times. Such a behavior has been observed through experiments (De Smedt et al., 1986; Toride et al., 2003).

4.3. Adsorptive transport; variably saturated conditions

Adsorptive transport, such as transport of viruses and colloids, is of great importance in studies of porous media (Bradford and Torkzaban, 2008). Under variably saturated conditions, principal
interactions usually occur not only at the solid–wetting (SW) interfaces, but also at the nonwetting–wetting (NW) interfaces (Torkzaban et al., 2008). These interactions are greatly affected by the water content. Eqs. (8) and (11) show that the concentration of adsorbed solutes depends on specific interfacial areas, which, in turn, are functions of saturation. Fig. 7 shows the normalized total interfacial areas as a function of saturation (Model 1), together with capillary pressure-saturation as well as relative permeability-saturation curves. The slope of $k_r - S_w$ is larger at higher saturation. This is due to the fact that the nonwetting phase first occupies the larger pores (which have the most contribution to the conductivity of the phase), after which there is a considerable drop in conductivity of the wetting phase. Further decrease in saturation will only cause slight decrease in permeability of the wetting phase, since almost all larger and percolating pores are already drained. As shown in Fig. 7, the SW interfacial area decreases during drainage (interfaces associated with the fluid films are neglected). This is due to the invasion of pores by the nonwetting phase. Initially, under saturated conditions, there is no NW interface present. Thus, the area of NW interface starts at zero, and increases with decrease in saturation.

At any given saturation, the fluids distribution within the pores and thus the amount of SW and NW interfaces in each pore are neglected. This is due to the invasion of pores by the nonwetting phase. Initially, under saturated conditions, there is no NW interface present. Thus, the area of NW interface starts at zero, and increases with decrease in saturation.

At any given saturation, the fluids distribution within the pores and thus the amount of SW and NW interfaces in each pore are neglected. This is due to the invasion of pores by the nonwetting phase. Initially, under saturated conditions, there is no NW interface present. Thus, the area of NW interface starts at zero, and increases with decrease in saturation.

Table 2
Boundary concentrations at the left and bottom boundaries of Model 2, units for mobile solutes are in mmol dm$^{-1}$ pore water, denoted as mM.

<table>
<thead>
<tr>
<th>Boundary</th>
<th>DOC</th>
<th>NO$_3^-$</th>
<th>NH$_4^+$</th>
<th>PO$_4$</th>
<th>O$_2$</th>
<th>Fe$^{3+}$</th>
<th>SO$_4^{2-}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Seawater groundwater interface</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.05</td>
<td>0.0</td>
<td>28</td>
</tr>
<tr>
<td>Inland groundwater plume</td>
<td>1.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.1</td>
<td>0.0</td>
</tr>
</tbody>
</table>

Table 3
The reaction network for Model 2.

Primary redox reactions
Aerobic degradation

Denitrification

Fe(OH)$_3$ reduction

Sulfate reduction

Secondary redox reactions
Nitrification

Fe$^{2+}$ oxidation

Equilibrium sorption
P adsorption

Table 4
The kinetic/equilibrium formulations for Model 2.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Condition</th>
<th>Rates</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aerobic degradation</td>
<td>If $O_2 &gt; K_mO_2$</td>
<td>$K_{O_2} [DOC] / KimO_2$</td>
</tr>
<tr>
<td></td>
<td>else</td>
<td>$K_{O_2} [DOC] / KimO_2$ $K_{O_2} [DOC] / KimO_2$</td>
</tr>
<tr>
<td>Denitrification</td>
<td>If $O_2 &gt; K_mO_2$</td>
<td>$K_{O_2} [DOC] / KimO_2$</td>
</tr>
<tr>
<td></td>
<td>else if $NO_3 &gt; K_mNO_3$</td>
<td>$K_{NO_3} [NO_3] / KimNO_3$</td>
</tr>
<tr>
<td></td>
<td>else if $NO_3 &lt; K_mNO_3$</td>
<td>$K_{NO_3} [NO_3] / KimNO_3$</td>
</tr>
<tr>
<td>Fe(OH)$_3$ reduction</td>
<td>If $NO_3 &gt; K_mNO_3$</td>
<td>$K_{NO_3} [NO_3] / KimNO_3$</td>
</tr>
<tr>
<td></td>
<td>else if $Fe(OH)_3 &gt; K_mFe(OH)_3$</td>
<td>$K_{Fe(OH)_3} [Fe(OH)<em>3] / K</em>{Fe(OH)_3}$</td>
</tr>
<tr>
<td></td>
<td>else if $Fe(OH)_3 &lt; K_mFe(OH)_3$</td>
<td>$K_{Fe(OH)_3} [Fe(OH)<em>3] / K</em>{Fe(OH)_3}$</td>
</tr>
<tr>
<td>Sulfate reduction</td>
<td>If $Fe(OH)_3 &gt; K_mFe(OH)_3$</td>
<td>$K_{Fe(OH)_3} [Fe(OH)<em>3] / K</em>{Fe(OH)_3}$</td>
</tr>
<tr>
<td></td>
<td>else if $SO_4^{2-} &gt; K_mSO_4^{2-}$</td>
<td>$K_{SO_4^{2-}} [SO_4^{2-}] / K_{SO_4^{2-}}$</td>
</tr>
<tr>
<td></td>
<td>else if $SO_4^{2-} &lt; K_mSO_4^{2-}$</td>
<td>$K_{SO_4^{2-}} [SO_4^{2-}] / K_{SO_4^{2-}}$</td>
</tr>
<tr>
<td>Nitrification</td>
<td>$K_{NO_3}[NO_3]/[O_2]$</td>
<td>$K_{NO_3}[NO_2]/[NO_2]$</td>
</tr>
<tr>
<td>Fe$^{2+}$ oxidation</td>
<td>$K_{Fe^{2+}}[O_2]$</td>
<td>$K_{Fe^{2+}}[O_2]$</td>
</tr>
<tr>
<td>P adsorption</td>
<td>$K_{P,T}$</td>
<td>$P_{T}$</td>
</tr>
</tbody>
</table>
4.4. Saturated reactive transport; seawater-fresh water mixing interface

The reactive mixing between seawater and groundwater in coastal aquifers influences the water quality of submarine groundwater discharge. While these waters come into contact at the seawater groundwater interface by density driven flow, their chemical components dilute and react through dispersion. The interaction between intruding seawater and fresh groundwater causes series of degradation processes in the coastal aquifer (Michael et al., 2003). The multi-component reactive transport feature of PoreFlow permits to address the chemical interactions that occur at seawater groundwater interface. Here, we study these interactions near a hypothetical interface between intruding seawater and fresh groundwater at the pore scale level assuming that the transverse dispersion is the main hydraulic process controlling such mixing at this scale.

To do so, a 3D pore network model of the size $N_i = 301, N_j = N_k = 11$ is used (Model 2). The properties of the generated network are given in Table 1. The physical length of model domain is 300 mm, with a porosity value of 0.27 and permeability of 80 m/day. The model is assumed to be parallel to the freshwater–seawater interface along its length, with its lower boundary representing the seawater. Following the work of Slomp and Van Cappellen (2004) and Nick et al. (2013), we consider anoxic fresh water and oxic seawater conditions (Fig. 8). At the seawater boundary, seawater contains $O_2$ concentration of 0.2 mM and $SO_4$ of 28 mM. The model is initially saturated with fresh water. Then, water with the same density (1000 kg/m$^3$) and viscosity ($1 \times 10^{-5}$ Pa s) but with different chemical compositions is injected continuously through the left (inlet) boundary (Table 2).

The dissolved organic carbon (DOC) of input water is \((CH_2O)_{106} \cdot (NH_3)_1 \cdot (H_3PO_3)_z\), where $x, y, z$ represent the C:N:P ratios, set to 106:11:1. Similar to Spiteri et al. (2008a), we consider seven equilibrium/kinetic reactions which allows us to study transformation processes affecting dissolved organic carbon degradation in saturated groundwater. These transformation processes are: aerobic degradation, denitrification, nitrification, $Fe(OH)_3$ reduction, $SO_4^{2-}$ reduction, $Fe^{2+}$ oxidation and $PO_4$ adsorption onto $Fe(OH)_3$ (Table 3).

<table>
<thead>
<tr>
<th>$K_{DOC}$ s$^{-1}$</th>
<th>$K_{in}$ mM$^{-1}$ s$^{-1}$</th>
<th>$K_r$ s$^{-1}$</th>
<th>$K_{O_3}$ mM</th>
<th>$K_{SO_4}$ mM</th>
<th>$K_{Fe^{3+}}$ mmol dm$^{-3}$</th>
<th>$K_m$ mM</th>
<th>$K_d$ dm$^{-3}$ mmol$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$1.0 \times 10^{-7}$</td>
<td>$1.0 \times 10^{-4}$</td>
<td>$1.0 \times 10^{-4}$</td>
<td>$3.0 \times 10^{-2}$</td>
<td>$1.0 \times 10^{-3}$</td>
<td>20</td>
<td>1.6</td>
<td>100</td>
</tr>
</tbody>
</table>

Fig. 9. (a) DOC, (b) $O_2$, (c) $PO_4^{3-}$, and (d) $NO_3^-$ concentration profiles along the main flow path plotted after 1.86 pore volume. Units for mobile solutes are in mmol dm$^{-3}$ pore volume. Dashed lines are the profiles for the model with the velocity of 2.317 m/year and the solid lines represent the result of the model with velocity value of 0.464 m/year. The lines marked with the circular symbols represent the result for the nonreactive tracer.

### Table 5

Parameter values used for simulation of the DOC degradation. $K_{DOC}$ is the rate constant for decomposition of $(CH_2O)_{106} \cdot (NH_3)_1 \cdot (H_3PO_3)_z$; $K_{in}$ is the rate constant for $Fe^{2+}$ reoxidation; $K_r$ is the rate for $Fe^{3+}$ reduction; $K_{O_3}$, $K_{SO_4}$, $K_{Fe^{3+}}$, $K_m$ and $K_d$ are limiting concentrations of $O_2$, $NO_3^-$, $Fe(OH)_3$, and $SO_4^{2-}$ respectively; $K_d$ is the adsorption coefficient (Hunter et al., 1998).
average velocities of 2.317 and 0.464 m/yr are performed. The top and bottom boundaries are set as no flow boundaries. Initially the concentrations of all the species are set to zero. The aerobic degradation reaction rates is defined as given in Hunter et al. (1998) and listed in Table 4. The limiting concentration for electron acceptors and reaction rates are shown in Table 5. 

Fig. 9 shows the average concentration profiles along the main flow path for different components. The dissolved oxygen and sulphate diffuse laterally (from the lower boundary representing the seawater) into the domain and the reactive mixing zone width extends along the main flow path. Oxygen concentration level is found to be lower for the simulation with lower flow velocity. This is also reflected in breakthrough curves monitored at the outlet (Fig. 10). As both examples are advective dominated flow, the advance of tracer concentration through the lower boundary remains the same. This can be seen in the tracer concentration profiles (Fig. 9 – O2 concentration profile) and breakthrough curves for the tracer result (Fig. 10 – O2 breakthrough curve). Therefore, under these conditions the molecular diffusion effect on dispersion can be ignored.

As shown in Fig. 10, the oxygen concentration increases at early time until the DOC plume propagates. Soon after the DOC plume reaches the outlet boundary, the oxygen concentration decreases significantly. The sulfate plume travels nearly conservatively due to high concentration of this component in the system. 

Denitrification is limited, because initially there is no NO3− in the system and nitrification is relatively small and limited by the oxygen supply. Fe2+ oxidation is also controlled by the available dissolved oxygen. The DOC concentration reaching to the outlet for the case of lower velocity is much less than that of the case with higher flow velocity. While the velocity ratio between these two simulations is 5, the DOC mass flux ratio is greater than 15. Therefore, the DOC degradation is more effective in the model with lower velocity. Consequently N and P release rates are about 2 times larger for the higher velocity simulation. The NH4 produced in the system due to primary redox reactions is nitrified to NO3− when it comes in contact with the O2, which is dispersed.

**Table 6** Calcium carbonate equilibria at 25 °C (Koutsoukos and Kontoyannis, 1984).

<table>
<thead>
<tr>
<th>Equilibrium</th>
<th>K</th>
</tr>
</thead>
<tbody>
<tr>
<td>H2O=H+ + OH−</td>
<td>1.007 × 10⁻¹⁴</td>
</tr>
<tr>
<td>H+ + HCO3− ⇌ H2CO3</td>
<td>2.249 × 10⁶</td>
</tr>
<tr>
<td>H+ + CO3²⁻ ⇌ HCO3⁻</td>
<td>2.133 × 10¹⁰</td>
</tr>
<tr>
<td>Ca²⁺ + HCO3⁻ ⇌ CaHCO₃⁺</td>
<td>10.0</td>
</tr>
<tr>
<td>Ca²⁺ + OH− ⇌ CaOH⁺</td>
<td>19.95</td>
</tr>
<tr>
<td>CO₂(aq)=H₂CO₃</td>
<td>3.390 × 10⁻²</td>
</tr>
</tbody>
</table>

IAP is the ion activity product determined for the reaction (Chou et al., 1989), and a solute with pH of 3.0 into a network of size average velocity is 0.1 m/d. Due to dissolution of calcite, the IAP is more mobile PO4 and the Fe(OH)3 is available in the domain.

These results show that biochemical processes combined with flow and transport can have a substantial effect on the release of nutrients into SGD. Our main goal, however, is to illustrate the applicability of the PoreFlow for modeling reactive transport in subsurface environment.

4.5. Reactive transport; including porosity change

PoreFlow is capable of computing the change in porosity and the flow field due to the progress of chemical reactions (Raof et al., 2012). It can also be used to obtain the corresponding relationship between porosity and permeability. In this section, we simulate a reaction/dissolution problem including porosity changes. We consider dissolution of carbonate calcium, CaCO3, due to the injection of a low pH solution. This problem has various applications such as CO2 sequestration into a reservoir rock.

The calcium carbonate equilibria parameters (Koutsoukos and Kontoyannis, 1984) are given in Table 6. The dissolution of calcite has been proposed to occur via three parallel reactions (Plummer et al., 1978; Chou et al., 1989)

\[
\begin{align*}
\text{CaCO}_3(s) + H^+ &\rightleftharpoons \text{Ca}^{2+} + \text{HCO}_3^- \\
\text{CaCO}_3(s) + H_2\text{CO}_3 &\rightleftharpoons \text{Ca}^{2+} + 2\text{HCO}_3^- \\
\text{CaCO}_3(s) + &\rightleftharpoons \text{Ca}^{2+} + \text{CO}_3^{2-}
\end{align*}
\]

The reaction consumes H+, and releases Ca2+ and carbonate. The rate of calcite dissolution is described by a Transition State Theory (TST) rate law (Chou et al., 1989):

\[
\text{Rate} = A(k_1[\text{H}^+] + k_2[\text{H}_2\text{CO}_3] + k_3) \left(1 - \frac{\text{IAP}}{K_{eq}}\right),
\]

where \(k_1, k_2, k_3\) are the reaction rate constants (Li et al., 2008), \([\text{H}^+]\) and \([\text{H}_2\text{CO}_3]\) are the activities of hydrogen ion and carbonic acid, IAP is the ion activity product defined as \(a_{\text{Ca}^{2+}} a_{\text{CO}_3^{2-}}\), \(K_{eq}\) is the equilibrium constant for the reaction (Chou et al., 1989), and \(A\) is the reactive surface area. Eq. (22) is used to calculate the dissolution rate within a pore.

We use concentrations in equilibrium with CaCO3 as the initial conditions. The diffusion coefficient is set to 1.0 \(\times\) 10\(^{-9}\) [m\(^2\)/s] and average velocity is 0.1 [m/d]. Due to dissolution of calcite, the initial (equilibrium) pH is as high as 10. Subsequent injection of solute with pH of 3.0 into a network of size \(N_i = N_f = N_k = 10\) (Model 3) for 60 days caused the dissolution of calcite, and therefore, an increase in porosity. During the simulation, the radius of the pore throats (that affect permeability) and pore bodies (which affect the storage of chemical products) is changed at each time step due to the dissolution-precipitation processes. Having the dissolved/precipitated mass of solid-phases calculated at each time step, the change in pore volumes is calculated for each pore using density of each solid phase. Then, the radius of each pore is updated accordingly. The above procedure is repeated for each time increment to calculate the evolution of cement permeability during the degradation process. By averaging over the network domain at successive time steps, we calculate the evolution of porosity and permeability as chemical reactions progress. Dissolution of calcite causes an increase in pore throat sizes which have the most effect on permeability of the pore network. The initial pore throat size distribution together with the pore throat size distribution after dissolution simulation are shown in Fig. 11a. Fig. 11b shows the corresponding increase in permeability due to evolution in porosity. Results show a five-fold increase in permeability as a result of 5.0% increase in porosity.

5. Conclusion

In this study, we introduce a pore-scale modeling tool, PoreFlow, to quantify and describe the physical/chemical processes that govern the transport of both tracer and reactive/adsorptive solutes in (variably) saturated porous media. PoreFlow is a FORTRAN-90 modular package whose capabilities include the generation of random structure or user defined networks, simulation of drainage process, discretization of pore spaces on the basis of saturation state of each pore, and solving flow and transport of multi-component reactive solutes under saturated and variably saturated conditions, using several complex algorithms. The solute transport governing equations are solved applying a fully implicit numerical scheme. An efficient substitution methods is applied to make the algorithm computationally more effective and appropriate for parallel computations. In presence of the nonwetting phase, there are fluid–fluid (i.e., nonwetting–wetting) interfaces in addition to solid–fluid (i.e., solid–wetting) interfaces. The adsorption to fluid–fluid interfaces may occur in addition to adsorption to solid–fluid interfaces. Coupling with Biogeochemical Reaction Network Simulator (BRNS) make it possible to simulate complex system of equilibrium or kinetic reactions. The reactions can be heterogenous resulting in evolution of porosity and permeability of the porous structure.

We present results of various simulations showing the capability of PoreFlow to model reactive flow and transport in porous media. This helps understanding of the processes, to perform
upscaling, and to develop macroscale constitutive relations suitable as inputs for continuum scale models. These include the relationships between phase saturation and parameters such as capillary pressure ($P_c-S_w$ curve), interfacial area ($a-S_o$ curve), relative permeability ($k_r-S_w$ curve) and solute dispersivity ($\alpha-S_w$ curve), as well as the relationship between porosity and permeability ($\theta-k$ curve), and tortuosity or effective diffusion and porosity ($D_{eff}-\theta$ curve).

References


Plummer, L., Wigley, T., Parkhurst, D., 1978. The kinetics of calcite dissolution in CO2-water systems at 5 deg to 60 deg c and 0. 0 to 1. 0 atm CO2. American Journal of Science, 278.


