A perspective on applied geochemistry in porous media: Reactive transport modeling of geochemical dynamics and the interplay with flow phenomena and physical alteration

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Abstracts:

In many practical geochemical systems that are at the center of providing indispensable energy, resources and service to our society, (bio)geochemical reactions are coupled with other physical processes, such as multiphase flow, fracturing and deformation. Predictive understanding of

these processes in hosting and evolving porous media is the key to design reliable and sustainable practices. In this article, we provide a brief review of recent developments and applications of reactive transport modeling to study geochemically driven processes and alteration in porous media. We also provide a perspective on opportunities and challenges for continuously developing and expanding the role of this valuable methodology to advance fundamental understanding and transferable knowledge of various dynamic geochemical systems.

Keywords:

Porous media, reactive transport modeling, coupled processes, multi-scale

1. Introduction

Porous media represent a type of material structure that is widely found in natural and industrial systems (Wildenschild and Sheppard 2013). Characterization of porous media and studies of the coupled hydraulic, (biogeo)chemical, mechanical and thermal processes in them are a prime need for many applications (Czaja, Trukhan, and Müller 2009; Bryant and Thompson 2001; Khaled and Vafai 2003; Berkowitz et al. 2016; Bultreys, De Boever, and Cnudde 2016; Nagel et al. 2016), which has united and fostered a growing community, such as interpore. One group of important practical applications involves porous geo-materials in the subsurface, including geologic storage of CO_2 and nuclear wastes, geothermal extraction, conventional/unconventional oil and gas production, groundwater pumping and remediation, and mining of mineral resources (Gallup 2009; Werth et al. 2010; McCartney, Sánchez, and Tomac 2016; Celia 2017; Hang Deng et al. 2021). Designing engineering practices for and assessing performance and environmental impacts of these systems require predictive understanding of fluid flow, mass transport, biogeo- and hydrogeochemical transformations and heat transfer in the evolving porous media.

Reactive transport modeling is the use of process-based models that offers predictive capability for the transport of reactive solutes in fractured and porous media, while being able to account for the changes in porous media structures and the coupling of biogeochemical and hydraulic processes, and increasingly the coupling with thermal and mechanical processes as well (Hang Deng et al. 2021; C. I. Steefel et al. 2015). Reactive transport modeling has been extensively used to enhance understandings of transport phenomena and geochemical reactions, and how they induce porous medium evolution in a wide variety of geochemical systems (Aradóttir et al. 2012; Alt-Epping et al. 2013; Xiong et al. 2021; Kruisdijk and van Breukelen 2021; Li et al. 2017; Thullner and Regnier 2020; Dai et al. 2020).

An important theme of reactive transport modeling in porous media over the past decade and many years to come - and of the studies of a variety of geochemical systems and dynamics in general - is the coupling of multiphysics and multiple scales (Fig. 1). Different chemical-physical processes have different characteristic time and length scales. For instance, aqueous reactions are in most cases instantaneous, whereas mineral reactions or biogeochemical transformations have rates that span over several orders of magnitude (A. F.

White and Brantley 1995; Palandri et al. 2004; Thullner, Van Cappellen, and Regnier 2005; Oelkers et al. 2018; X. Zhang et al. 2021). Similarly, flow rate can vary significantly depending on whether elevated pressure gradient is imposed. The scales of these processes may also be correlated with the length scales of the pore structures and other chemical-physical properties. In geo-materials, pore sizes can vary between nanometer (e.g., in shales and coals, the typical pore sizes of which are < 50nm (Zhu et al. 2021)) and millimeter, while features such as fractures can have length scales of meters to hundreds of meters (H. Deng and Spycher 2019). In clay minerals where nano- and micro-pores are dominant, electrical double layers and electrochemistry become particularly relevant (C. I. Steefel and Tournassat 2021). This highlights that different processes can be dominant in different features, and hence they need to be coupled temporally and spatially.

In order to improve our ability to incorporate (biogeo)chemical-physical processes and properties of different scales that are important in controlling geochemical systems and dynamics of practical importance to our society, it is required to have detailed characterization data of the porous media (e.g., mineral abundances and accessibility (Hailin Deng et al. 2013; Qin and Beckingham 2021; Kim et al. 2022)), accessible computational resources, and most importantly verified reactive transport models. The development of such models relies on researchers who have deep knowledge of multiple disciplines including geochemistry, hydrology and beyond to conceptualize the physical problems, and have strong mathematical background to build the mathematical models and develop the numerical solutions. In recent years, the community of reactive transport modeling, as illustrated by the works in this special issue and those cited in this article, is growing.

In this perspective paper, we provide a summary of recent progress in modeling of coupled processes in porous media in the context of practical geochemical systems. It is not meant to be exhaustive. We focus on examples from three major types of models and discuss their respective advantages in addressing different scientific needs and limitations. We also provide a discussion of the opportunities and challenges of continuously deepening our understanding of practical geochemical systems, especially via reactive transport modeling in porous media.

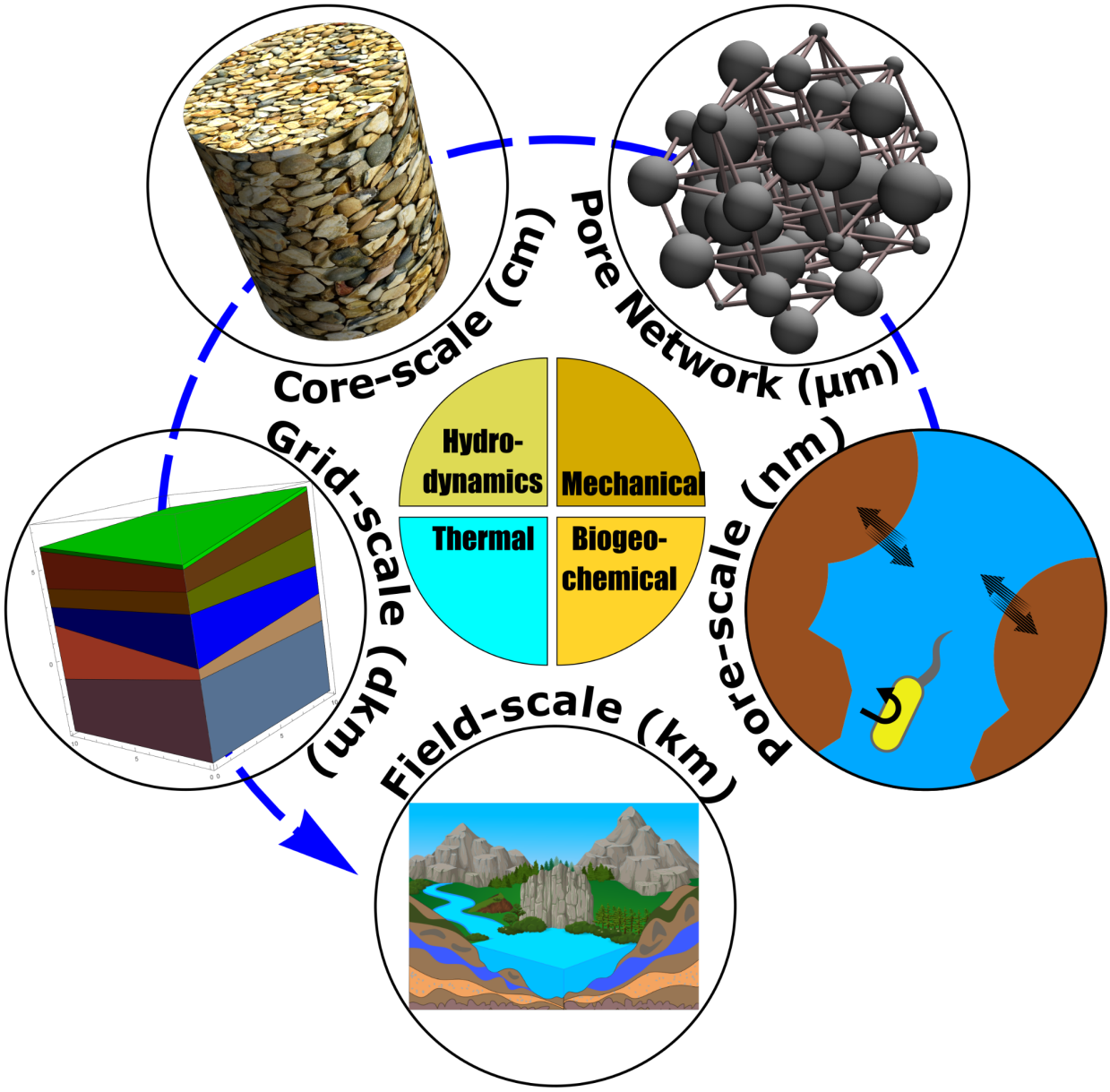

Figure 1: General upscaling sequence from pore-scale to field-scale. Separate characteristics of the medium are determined at different scales alone or in combination.
Incorporation of the data together leads to development of a static map of the media which serves as base for simulating flow and transport (modified after Blunt et al. (2013) and Hajizadeh et al. (2011)).

2. Pore-scale and pore network models

A predominant characteristic of random porous environments which influences the macroscopic transport of fluids, chemical species and their distribution, is the spatial heterogeneity that exists at various scales. The intrinsic level of spatial heterogeneity determines the degree at which different fluids come to contact (e.g., a miscible injection process in a hydrocarbon reservoir) or the fluids and the solid phases interact (e.g., the accessibility of microbial aggregations to organic contaminants in a bio-remediation process), which in turn may alter the efficiency of e.g., hydrocarbon recovery or bio-degradation. To this end, having access to an accurate model that could explicitly represent the geometry and topology of the pore space is of crucial importance.

Several techniques have been developed over the past years, to characterize the pore space and provide its geometrical, topological, and mineralogical information for simulating physical and geochemical processes. Compared to methods such as mercury intrusion porosimetry (Giesche 2006; Rouquerol et al. 2012) and gas adsorption (Sing 1989; Fu et al. 2021), non-destructive X-ray computed microtomography or micro-CT (Berg et al. 2013; Cnudde and Boone 2013; Noiriel 2015; Silin et al. 2011) has enabled the direct imaging of three dimensional pore structures of small rock samples with ever-increasing spatial and temporal resolutions. Pore structural information constructed by direct imaging techniques, typically exists as three-dimensional voxel-based binary grid representations of pores and grains. It should, however, be acknowledged that given the multi-scale nature of geo-materials, sub-resolution features may still exist even though the resolution of image instruments has been extended to sub-micron and nanometer (Schlüter et al. 2014). A comprehensive review of the various pore space characterization techniques has been given by (Sadeghnejad, Enzmann, and Kersten 2021) in our special issue and (Blunt et al. 2013).

Although the 3D imaging techniques have provided a breakthrough in pore space characterization methods, they do however, suffer some limitations. There is always a trade-off between the achievable high resolution of the direct measurements and the sample size. The highest resolution in the literature is reported from synchrotron CT, but the samples need to be rather small to achieve these resolutions. Consequently, although these images have high resolutions to appropriately define the interior structure of the medium, the small domain size poses uncertainty in their statistical representativeness and hence modeling accuracy. The 3D imaging tools are also expensive and the apparatus may not be readily available.
High-resolution two dimensional pore space data, on the other hand, can be conveniently obtained by application of available scanning electron microscopy (SEM) to thin sections of rock or soil samples. Then a 3D pore space representation can be reconstructed from the information contained in 2D section images (Hajizadeh and Farhadpour 2012; L. E. Beckingham et al. 2013). The use of SEM energy-dispersive X-ray spectroscopy and other microscopic and spectroscopic techniques have also allowed detailed mineralogical characterizations that complement morphological data from CT images (Kim et al. 2022; B. R. Ellis and Peters 2016; Peters 2009).

From a flow and reactive transport perspective, solving the governing equations on pore space images is possible. These methods are collectively referred to as Direct Numerical Simulations (DNS), and in the context of geological applications the term ‘computational

microfluidics for geosciences' has been recently proposed (Soulaine, Maes, and Roman 2021). The challenge in these numerical techniques consist in describing accurately the interfacial conditions at the fluid-mineral and fluid-fluid interfaces. Indeed, these boundaries move with hydrodynamic forces (for two-fluid systems) and surface reactions (e.g. for mineral dissolution or precipitation). Computational fluid dynamics (CFD) methods such as level set (LS) (Prodanovic, Bryant, and Karpyn 2010; Jettestuen, Helland, and Prodanović 2013) and Volume of Fluid (VoF) methods (A. Q. Raeini 2013) have recently been used to solve conservation equations of mass and momentum at the pore scale (P. Mostaghimi, Bijeljic, and Blunt 2012; Peyman Mostaghimi, Blunt, and Bijeljic 2013; Shams 2018; P. Li, Deng, and Molins 2022; Molins et al. 2021). Several approaches also exist to approximate Navier-Stokes solutions in the pore-space, e.g., particle tracking approaches such as the Lattice Boltzmann method and the Smoothed Particle Hydrodynamics (SPH) method (Chen et al. 2018; Hao and Cheng 2010; Dou and Zhou 2013; Yoon, Kang, and Valocchi 2015). However, these methods are computationally demanding and require the employment of high computational resources using parallel computation. There are therefore rooms for further research to accelerate these voxel-based methodologies particularly to simulate the mesoscopic scale phenomena and inter-pore interactions.

An alternative is to use pore network models (PNM) to solve the flow and reactive solute transport (Fig. 2). A pore network is a system of pores connected to each other by throats, usually with idealized geometries to focus on the complex structure of the porous medium (Fatt 1956; Dupin, Kitanidis, and McCarty 2001; Acharya, Van der Zee, and Leijnse 2005). They can be constructed directly using *a priori* distributions of pore/throat length and diameter or using information extracted from voxel-based images obtained experimentally (Vogel, Weller, and Schlüter 2010). While the former can be used to generate both regular (Thullner, Zeyer, and Kinzelbach 2002; Ezeuko et al. 2011; Gharasoo et al. 2012; Rosenzweig, Furman, and Shavit 2013) and irregular network models (Jamshidi, Boozarjomehry, and Pishvaie 2009), the latter method generates sample specific networks that are topologically disordered (Dong and Blunt 2009; Rabbani, Jamshidi, and Salehi 2014). When a 3D image is available, pore networks can be directly extracted (Al-Kharusi and Blunt 2008; Dong and Blunt 2009; Gharedaghloo et al. 2018), which preserves the intricacy of the pore structure most truthfully. It has been shown that the 2D images are reasonably informative in some cases and can be utilized to approximate the 3D connectivity of the actual media with high degree of reliability (Rabbani et al. 2016). This is particularly true if the assumption of stationarity is valid. For a particular application, the reliability of pore network modeling mainly depends on the accuracy of the network in representing the geometrical (e.g. throat length, cross section) and topological (pore to throat connections) characteristics of the actual pore space (Hajizadeh, Safekordi, and Farhadpour 2011), as well as the relations used to map the physics of the actual pore space to the simplified geometry.

Pore scale and pore network models also provide valuable insights for the upscaling of flow, transport and geochemical properties from pore scale to Darcy or continuum scale (Hang Deng et al. 2018; Tartakovsky et al. 2013). Examples include the upscaling of the transport and deposition of nano-particles in porous media (Seetha et al. 2017), sorption (A. Raoof et al. 2013), bioclogging (Thullner, Zeyer, and Kinzelbach 2002; Surasani et al. 2013; Lopez-Peña, Meulenbroek, and Vermolen 2018, 2019), mineral reaction rate (Li Li, Peters, and Celia 2006), permeability changes arising from mineral reactions (Nogues et al. 2013), or multiphase flow in

the rocks (Hajizadeh, Safekordi, and Farhadpour 2011; Joekar-Niasar and Hassanizadeh 2012). In the remainder of this section, we highlight a few application examples.

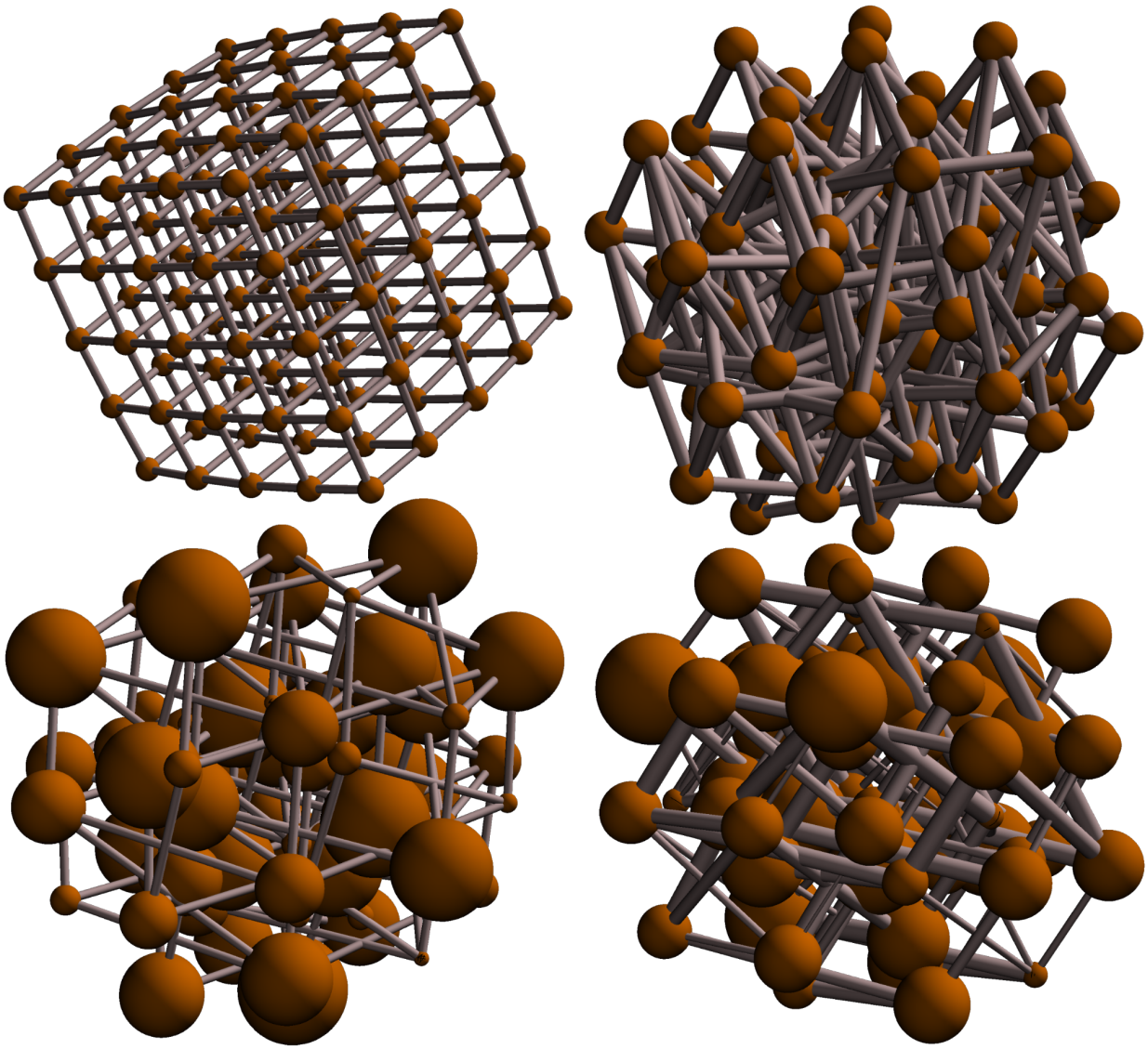

Figure 2: A schematic view of the 3D constructed pore network models. Top-Left: Regular pore network in which the pore bodies and throat lengths are identical. Note that pore throats radii

are identical. Different radii sizes can be assigned to the pore throats either permanently (e.g., Dupin et al., 2001; Gharasoo et al., 2012) or dynamically (e.g., due to biofilm growth Thullner et al., 2002, 2008; Ezeuko et al., 2011; Lopez-Peña et al., 2019). Top-Right: Irregular pore network in which pore bodies are identical but the pore throats with various lengths connect the adjacent pore bodies (Raouf and Hassanizadeh, 2010). Down-Left: Irregular pore network with random sizes of pore bodies connected randomly with pore throats of various length, generated using statistical a-priori distribution or L-system method (Jamshidi et al., 2009). Down-Right: Pore networks extracted from the real 3D pore images.

2.1 Two-phase flow

Two-phase or multiphase flow is common in many geochemical systems, such as unsaturated soils and geological carbon storage reservoirs. Pore-scale models provide a valuable tool to study the flow patterns (Zhao et al. 2019). For example, (Liu, Zhang, and Valocchi 2015) utilized the pore scale modeling approach to study the influential parameters on flow patterns, such as viscosity ratio, capillary number, and media heterogeneity on the two-phase immiscible displacement in a realistic, heterogeneous microfluidic flow cell. (Tang et al. 2019; Zacharoudiou, Boek, and Crawshaw 2018) used Lattice Boltzmann method to simulate the CO_2 displacement on a number of three-dimensional micro-CT images (Ketton limestone or sandstone) during the drainage process. The results helped with identifying the factors contributing to CO_2 displacement efficiency. (Bakhshian and Sahimi 2017) extended the pore-scale modeling of immiscible displacement of brine with supercritical CO_2, to investigate the effect of wettability heterogeneity (or fractional-wettability conditions) during the immiscible injection of CO_2 and its capillary trapping after the injection. Another interesting topic that can be covered by pore-scale modeling and has been largely overlooked in the community is coal-bed methane recovery where the penetration of CO_2 into coal is driven by stress-enhanced diffusion (Vermolen et al. 2009).

The use of pore scale models for flows at very low capillary number ($\delta \leq 10^{-5}$) which is known as capillary dominated flow or quasi-static flow has been limited due to the numerical artifacts of spurious currents (Abadie, Aubin, and Legendre 2015). Another important feature in two-phase flow is the water film at the solid surface, which is described in most advanced simulators using lubrication models (Pahlavan et al. 2018; Abu-Al-Saud et al. 2020). Through the concept of disjoining pressure, these models directly account for intermolecular forces that are related to van der Waals interactions and electrical double layers, and get rid of the notion of contact angle to describe wettability properties.

Pore network models provide an important tool for larger scale investigations and for upscaling. (Valvatne et al., n.d.) estimated the single-phase and multiphase properties for a number of water-oil and mixed-wet samples using a predictive pore network. They matched the mercury injection capillary pressure using adjustments to pore size distribution of the samples. Then predictions of single and multiphase properties were made with no further adjustments to the model. Later, the pore network models were extended to model the viscous force dominated flow or dynamic pore scale modeling (Bagudu, McDougall, and Mackay 2015; Dahle and Celia 1999). (Ali Q. Raeini, Bijeljic, and Blunt 2018) investigated the capillary-dominated two-phase flow to estimate the averaged flow properties including relative permeability and capillary pressure using the generalized network described previously in (Ali Q. Raeini, Bijeljic, and Blunt

2017). They considered the effects from gravity and viscous forces as a perturbation to estimate the local capillary pressures throughout the network. They reported successful predictions of entry capillary pressure for a number of contact angle values, aspect ratio and geometry.

2.2 Biogeochemical reactions

Within the realm of reactive transport modeling, pore scale modeling has been used to estimate spatially resolved reaction rates at the pore scale, rather than relying on macroscopic averages (Amir Raoof and Majid Hassanizadeh 2010; Gharasoo et al. 2012; Hang Deng et al. 2018; Molins et al. 2021). The evolution of pore structure during chemical, electrochemical or bacterial effects also have been modeled (Xie et al. 2017; Molins et al. 2021). The evolution of the pore space potentially leads to modifications in the macroscopic transport properties, such as permeability and diffusivity (H. Deng et al. 2021). For example, (Dashtian et al. 2019) studied the pore scale advective, diffusive and reactive mechanisms of CO_2-enriched brine interactions with rock minerals to understand the effects of CO_2 mineral trapping on the morphological alterations in the pore structure. The reactive solute transport and dissolution was then used to predict the changes in petrophysical properties and pore space topology which is crucial in predicting the long-term security of CO_2 storage in underground formations.

A key and challenging aspect of two-phase pore-scale simulations in reactive systems is to describe wettability alteration, which is a result of the complex interplay between surface roughness, surface chemistry, and compositions of the fluid phases. To account for such an effect, a strong coupling between geochemical models and two-phase transport models at the pore-scale is required (Maes and Geiger 2018). It is also important to account for mass transfer across fluid-fluid interfaces and the subsequent changes in phase compositions. Novel numerical techniques including the Continuous Species Transfer allow tracking of the phase composition in a two-fluid system with thermodynamic conditions at the fluid-fluid interface (Maes and Soulaine 2018).

Transport mechanisms in the biodegradation processes are often coupled with permeation of water or aqueous solutions, diffusion of gaseous compounds and sorption of ionic contaminated water. In this context, (Jung and Meile 2019) demonstrated that effective reaction rates and flow behavior in the hosting media is directly correlated with its micro-structure. Effects from porous medium structure and pore-scale heterogeneities on the biodegradation of contaminants (Gharasoo et al. 2012), the isothermal evaporation of brine and salt precipitation (Lehmann and Or 2013), the formation of microbial patterns (Gharasoo et al. 2014), and the switching of microbes between active/inactive states (Stolpovsky, Gharasoo, and Thullner 2012) are also explored.

Similar approaches in using pore network models were taken to investigate the effect of bioclogging on hydraulic properties of a medium (Suchomel, Chen, and Allen 1998; Dupin, Kitanidis, and McCarty 2001; Thullner and Baveye 2008; Ezeuko et al. 2011). These authors explored the evolution of hydrodynamics as a result of the development of a biofilm growth in the pores for different biofilm properties, and some also introduced a porosity-permeability relationships for bioactive media as an alternative to the Kozeny-Carman equation (Thullner, Zeyer, and Kinzelbach 2002; Lopez-Peña, Meulenbroek, and Vermolen 2018). There has been recently a significant increase in the number of biogeochemical reaction models describing the

intrinsic microbial behavior in more details (e.g., (Mellage et al. 2015; Gharasoo, Thullner, and Elsner 2017; Ehrl, Gharasoo, and Elsner 2018; Gharasoo et al. 2019; Khurana et al. 2022a)) that can be implemented into pore-scale models in order to realistically simulate natural attenuation of compounds in porous environments. The same concept of coupling pore-scale models with more detailed and advanced reaction kinetics can be extended to other fields such as, CO_2-methane exchange in gas-hydrate sediments for gas recovery (Gharasoo, Babaei, and Haeckel 2019), aerobic and anaerobic CO_2 respiration in soil (Davidson et al. 2012; Pagel et al. 2014), inhibitory effects of electron acceptors and donors in soil bioremediation (S. Zhang, Gedalanga, and Mahendra 2016), and the depletion of light non-aqueous phase liquids (LNAPL) in natural zones (Sookhak Lari et al. 2019).

Unsaturated reactive transport in porous media has been the holy grail of groundwater studies where the redox processes play a deterministic role in the fate of nutrients (Golparvar, Kästner, and Thullner 2021; Pot et al. 2022). Oxygen as the main oxidant for the aerobic organisms diffuses from the gaseous phase into the aqueous phase. Lack of the oxygen in water-saturated zones activates anaerobic bacteria that consume other available electron acceptors such as nitrate and sulfate for their catabolic activities. Most of the studies in this field use macroscopic unsaturated solute transport models that solve Richard's equation (Richards 1931; van Genuchten 1980) at continuum scale, such as HYDRUS-PHREEQC (Jacques et al. 2018) and MIN3P (Mayer, Frind, and Blowes 2002; Sihota and Ulrich Mayer 2012). Therefore, lack of a sophisticated unsaturated reactive pore-network model has been noted in which the redox processes are linked to the variability of water saturation in pores, and the reduction-oxidation reactions are mainly regulated by soil water content, next to other soil properties (Golparvar, Kästner, and Thullner 2021).

2.3 Pore-scale applications in deforming media

Geochemical reactions can trigger complex mechanical changes in the porous media. For example, (Noiriel 2015) used X-ray microtomography to show that dissolution and precipitation reactions can lead to particle displacement and migration. It was also experimentally illustrated that pore-scale deformation can affect properties such as porosity and permeability (Kang et al. 2014; Yoon et al. 2012; Spokas et al. 2019).

There is, however, relatively limited pore-scale work on rock deformation. Swelling and deformation of porous structure as the result of sorption has been studied using pore network modeling. The model of (Bakhshian and Sahimi 2017) calculates the sorption between the solid matrix of the porous medium and the adsorbing fluid by considering the elastic energy stored in the medium and the energy interactions between the adsorbates. The model successfully captured the changes in the sample porosity by properly reproducing the dependence of the strain on the bulk pressure, providing insights into the porous medium deformations as a result of CO_2 sequestration.

3. Micro-continuum-scale Models

Pore scale models introduced in the previous section clearly distinguish between the solid phase and the pore space, and provide a more accurate description of the coupled chemical-physical processes in the pore space and at the solid-fluid interfaces. Therefore, pore-scale models are typically more reliable for predictive modeling. However, they are in general computationally expensive and their applications are limited to relatively small computational domains (~1cm). The trade-off between domain size and resolution also means that sub-grid resolution properties – such as micro-porosity - and processes which can be important especially in nanoporous media are un-resolved. Another challenge of the pore-scale model is tracking the movement of the solid-fluid interface as a result of mineral dissolution or crystal growth. For mineral precipitation in which the location of nucleation can be random or in the solution, interface tracking (e.g., the embedded boundary method or level set method (Molins et al. 2021)) becomes difficult. While pore network models can be used to address the challenge of computational costs and sub-resolution porosity, they simplify pore geometries and thus pore-scale heterogeneity.

Continuum scale models, as well be discussed in more detail in the next section, rely on homogenized equations (e.g., Darcy's law for flow), averaged parameters (e.g., porosity, permeability and reactive surface area) at the scale of representative elementary volumes (REV), and constitutive relations that are largely empirical. Therefore, while continuum scale models can be used for simulations at large scale, uncertainties may be introduced in predictions as the parameters and constitutive relations calibrated for one case do not necessarily hold for another.

Therefore, for accurate and efficient predictive modeling, it is necessary to develop multi-scale strategies that can simultaneously capture important processes with different characteristic length and time scales, in addition to upscaling via constitutive relations developed based on high fidelity models at the finer scale. Two categories of multi-scale approaches have seen significant growth in the past decades: hybrid models and micro-continuum models (X. Yang et al. 2021). Hybrid models involve domain decomposition, selection and application of different models (different sets of governing equations) for each subdomain, and continuity check at the boundaries between sub-domains (Battiato et al. 2011).

Micro-continuum models typically include a pore-scale domain and a porous domain that are distinguished by the local porosity (ϕ), and a single set of governing equations is solved for the entire computational domain (Soulaine and Tchelepi 2016; Noiriel and Soulaine 2021).The local porosity is 1 in the pore space, is zero in the impermeable solid phase, and can be a fraction value at the solid-fluid interface or in the permeable solid phase where there is microporosity. While the micro-continuum model can be used as a pore-scale model by setting a zero porosity in the solid phase (Molins et al. 2021), it distincts itself from the pore scale models by how the interface is captured. In this case, the surface area of the interface within a grid block is estimated as the gradient of the local porosity. This formulation makes it easy to track the movement of the interface as a result of mineral dissolution and precipitation. The micro-continuum scale models also differ from the pore-scale model for its capability of simultaneously considering porous matrices. In this mode, the surface area in the porous domain can be parameterized by specific or bulk surface area as in the continuum scale model. This means explicitly modeling of open fractures and bordering matrices and at a smaller scale

of sub-resolution features such as micro-porosity. The local porosity field can be derived readily from micro-CT data, by mapping the grayscale to local porosity without requiring segmentation that can involve information loss and introduction of segmentation errors (Soulaine et al. 2016).

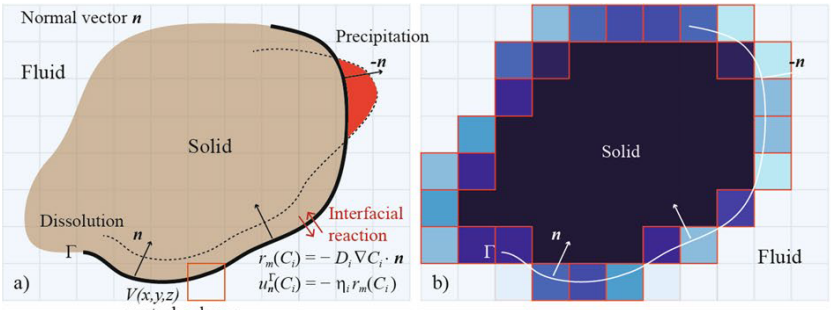

Figure 3: conceptual illustration of the micro-continuum scale model, including the local porosity and relationship with the pore-scale model. (Noiriel and Soulaine, 2021）

3.1 micro-continuum scale modeling of flow

In micro-continuum scale modeling, the flow is typically described by the Darcy-Brinkman-Stokes (DBS) equation. In the seminal paper of (Brinkman 1949), Darcy's equation was modified in order to account for the viscous force exerted by the fluid flow on the particles, which can be important in very porous media. The modification basically involves combining the pressure gradient from Darcy's law and that from the Stokes equation but with an adjusted viscosity for the latter. In later works, such as (Whitaker 1986), it was demonstrated that similar forms can be derived from volume averaging of the pore-scale equations. As such, conservation is satisfied at the boundary between the pore-scale and porous domains.

This approach is particularly useful when the solid phase is micro-porous or nano-porous. (Soulaine et al. 2016) used the Darcy-Brinkman approach to examine the impacts of micro-porosity on the permeability of a Berea sandstone, and showed that even with a 2% microporosity, flow distribution and permeability tensor are significantly affected. (Guo, Ma, and Tchelepi 2018) used the DBS equation to simulate gas flow in organic-rich shales based on focused ion beam scanning electron microscopy (FIB-SEM) images, with modifications that account for non-Darcy effects (e.g., slip flow) and surface diffusion.

The micro-continuum approach has also been extended to more complex fluid systems. For instance, (Soulaine, Creux, and Tchelepi 2019) developed the multiphase capability based on the DBS approach, in which multiphase flow is described by the relative permeability in the porous domain and is dictated by the surface tension force in the pore domain. The approach has been extended in (Carrillo, Bourg, and Soulaine 2020) to account for capillary effects within the porous domain as well. It enables two-phase flow simulations in 3D micro-CT images containing sub-voxel porosity (Carrillo, Soulaine, and Bourg 2022). In (Guo, Mehmani, and Tchelepi 2019), a multi-scale framework was developed for compressible flow, in which the DBS approach is an important component that ensures consistency at the boundaries between the pore domain and porous domain.

3.2 micro-continuum scale modeling of reactive transport processes

From a geochemical perspective, one important advantage of a micro-continuum reactive transport model is its ability to integrate high-resolution geochemical and mineralogical

data, in addition to spatially resolved physical properties that control flow (Carl I. Steefel, Beckingham, and Landrot 2015). (Kim et al. 2022) in this special issue serves as an example of combining synchrotron-based techniques and machine learning algorithms to acquire mineralogical data, allowing identification of multiple mineral phases in a single pixel. Micro-continuum scale reactive transport models provide a tool that investigates and quantifies how these small scale chemical (e.g., mineral composition) and physical heterogeneities (micro-porosity) can affect solute transport and system evolution in relatively large domains. For example, (Jung and Meile 2021) have shown that consideration of biofilm porosity leads to prediction of more uniform biofilm development in porous media. (Yan et al. 2018) reported strong impact of micro-scale water distribution on microbial organic carbon decomposition in unsaturated soils. The DBS-based micro-continuum modeling results of (Soulaine, Creux, and Tchelepi 2019) demonstrated that in shales it is important to account for the spatial distribution of kerogen and clays in relation to micro-cracks in order to accurately predict hydrocarbon production. (Q. Zhang et al., n.d.) applied the DBS-based micro-continuum reactive transport model to examine reactive transport processes in an altered porous layer bordering an open fracture and the less porous intact rock matrix, which develops as a result of mineral compositional heterogeneity. The results highlighted that ignoring advection in the altered layer as would be the case if a pore-scale scale is used for modeling the fracture, important chemical gradients that will influence fracture alteration in the long run would be overlooked.

One important application of the micro-continuum scale approach is the modeling of wormholing and channelization. Wormholing (or channelization) is a self-organization phenomenon that develops as a result of positive feedback between preferential flow and mineral dissolution in porous media (or fractures). Pore scale description is required in the wormholes or channels, because the development of hydrodynamic boundary layer can result in large concentration gradients (Szymczak and Ladd 2009) where the well-mixed assumption of the continuum-scale models will break down. Comparison of simulation results using a continuum approach versus a micro-continuum approach has also shown differences in the shape and temporal evolution of the wormholes (Ormond and Ortoleva 2000). In fractures, when the bordering rock is impermeable, a pore-scale model can be used to simulate channelization (Vitaliy Starchenko, Marra, and Ladd 2016). Otherwise, consideration of the porous domain can be critical. For instance, in the experimental study of (Dávila et al. 2016), wormholes can bypass the fracture and form in the porous rock instead. In these cases, micro-continuum modeling will be necessary. Systematic investigations have been performed using the micro-continuum approach to examine different regimes of wormhole development and their dependence on Peclet number and Damkohler number (Golfier et al. 2002; Soulaine et al. 2017; You and Lee 2021).

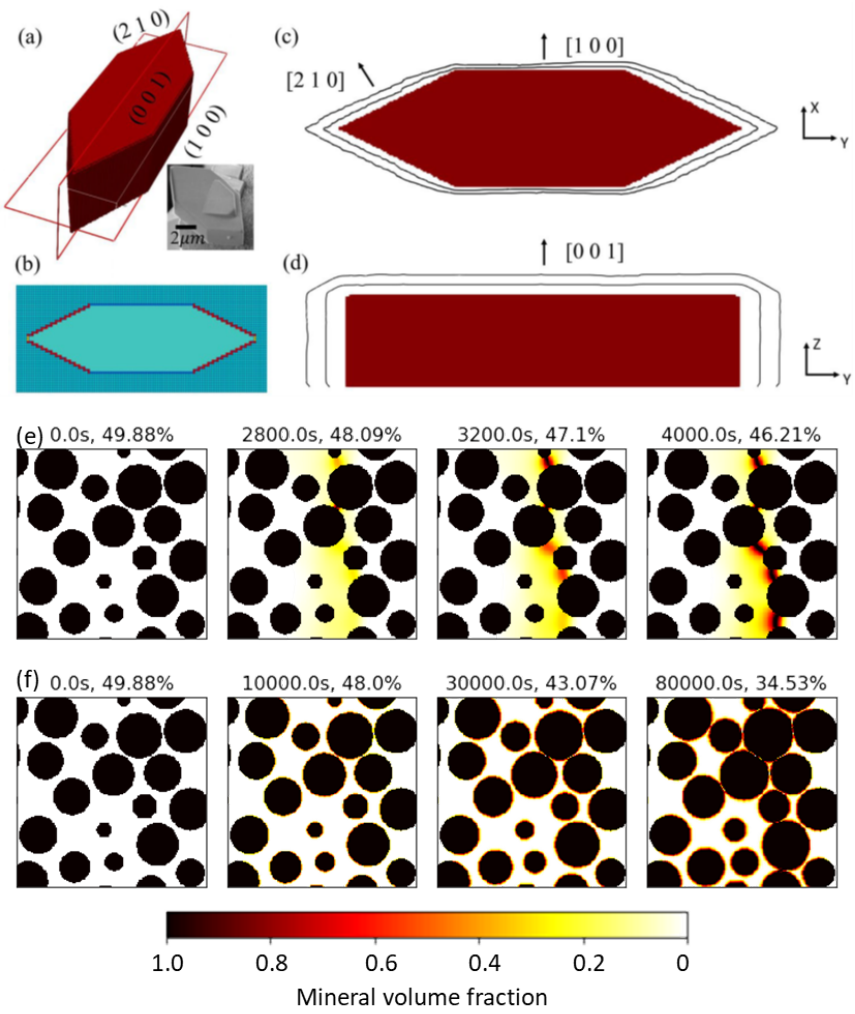

Figure 4: (a)-(d) micro-continuum modeling of growth of a single crystal (Yang et al., 2021). (a) is the experimentally observed barite crystal, (b) illustration of reaction rate specific to the crystal orientation, (c) and (d) are contours at hour 3 and 6 at the x-y and y-z plane, respectively. (e) and (f) show snapshots of barite precipitates in porous media due to homogeneous nucleation and crystal growth, respectively. (Deng et al., 2021)

Another important application of the micro-continuum reactive transport model is the modeling of precipitation processes. Recent development and application of micro-continuum reactive transport models have also included considerations of improved precipitation dynamics. (F. Yang, Stack, and Starchenko 2021) implemented reaction rates that are dependent on crystallographic orientations, and were able to reproduce the shape of crystals observed experimentally. (H. Deng et al. 2021) modeled precipitation in diffusion-dominated porous media as crystal growth on the solid-fluid interface and homogeneous nucleation in the solution based on the Classical Nucleation Theory. The modeling results reproduced precipitation patterns observed in previous experimental studies (Noiriel et al. 2012; Rajyaguru et al. 2019), and were used to upscale precipitation driven pore structure alteration to continuum-scale diffusivity changes. (H. Deng, Poonoosamy, and Molins 2022) in this special issue used a micro-continuum reactive transport model to reproduce precipitation patterns and the dependence on fluid saturation that were observed in previous experiments but not captured by

the continuum scale model. The study has further expanded the modeling capability by combining probabilistic nucleation with the CNT, which provides the means to examine the textures of precipitations (Vitalii Starchenko 2022).

The micron-continuum modeling approach has also been used to study Microbially Induced Calcium carbonate Precipitation (MICP) - a promising technique to stabilize soil, seal leaky wells, immobilize contaminants, and control permeability in porous and fractured media (Minto et al. 2018; Minto, Lunn, and El Mountassir 2019). In (Minto et al. 2018), the micro-continuum approach was used to simulate core-scale structural and flow changes caused by MICP, considering the evolution of bacteria concentration and their attachment/detachment to the mineral surfaces. A micro-continuum scale model was further developed to investigate field scale MICP practices, including domains of open fractures and continuum matrices between injection and extraction wells (Minto, Lunn, and El Mountassir 2019).

3.3 micro-continuum scale modeling of other physical processes

The framework of the micro-continuum models makes it relatively easy to integrate the equations of continuum mechanics. For instance, (Carrillo and Bourg 2019, n.d.) expanded the micro-continuum approach to consider flow induced deformation and cracking, and to investigate clay swelling and the resulting permeability in relation to clay fraction. This also confirms that micro-continuum reactive transport models provide a promising option for developing fully coupled chemical-mechanical codes.

4. Continuum-scale Models

The continuum formulation of reactive transport in porous media involves averaging over the representative elementary volume (REV), which incorporates micro-scale information about pore sizes, mineral grain sizes, mineral compositions, etc. into a continuum scale (mm scale to m scale) REV (Bear 1972). The continuum-scale reactive and transport equations include various effective constitutive parameters such as permeability, tortuosity, dispersivity, mineral compositions, reaction rate constant (k), equilibrium constant (K), specific mineral surface area, etc (Lichtner and Kang 2007). One important aspect of performing continuum-scale simulations is to obtain justified values for these constitutive parameters, sometimes through upscaling of micro-scale models. Continuum-scale reactive transport modeling has been widely used in geologic CO_2 storage, environmental remediation, and geothermal production applications, and studies of watershed biogeochemistry.

4.1 Geologic CO_2 storage applications

For geologic CO_2 storage, mineral trapping is an important mechanism that determines the long-term fate of injected CO_2. Quantitative determination of the amount of CO_2 trapped in mineral phases typically requires a field-scale continuum reactive transport model to simulate the interactions between CO_2 and the host rock. Some works (e.g., Xu et al., 2004; Zhang and DePaolo, 2016) calculated the conversion

efficiency of CO_2 into carbonates with the application of continuum-scale models over a very long CO_2 storage period (i.e., 1000 to 100,000 years), showing a CO_2 mineral trapping capacity of about 90 kg/m^3 porous media. The major CO_2 trapping minerals are dawsonite, ankerite, magnesite and siderite. The CO_2 mineral trapping capacity obtained is helpful for practitioners to determine the long-term CO_2 storage capacity. Also, relatively fast mineral dissolution and precipitation in flow channels (e.g., joints, fractures, etc.) within the host rock and the caprock may change the overall permeability of the system and thus influence the migration behavior of the injected CO_2 and displaced brine (Zhang et al., 2022).

Two important factors, impurity in the injected CO_2 stream and pH buffering capacity of the host rock, may have an impact on CO_2 storage modeling and need to be incorporated into the continuum-scale reactive transport modeling. The injected CO_2 may contain small amounts of impurities like NO_2, SO_2 and N_2, and the target storage formation may contain other sour gases like H_2S (Brian R. Ellis, Crandell, and Peters 2010). Even a trace amount of impurities can affect the solubility of CO_2 and cause deviation of modeling results from the actual value. (Spycher et al. 2019) revealed that when impurities like SO_2 and NO_2 are incorporated in the model, they readily partition into the aqueous phase close to the injection well and further lower the pH, compared with the case of CO2 acidification only. As for pH buffering capacity, a host rock rich in feldspars and clay minerals can hinder the drop of pH after CO_2 injection, which slows down the reaction between CO_2 and the host rock (or caprock). In most cases, the pH buffering capacity reduces the risk of CO_2 penetration through the caprock, which is beneficial for long-term CO_2 storage (Wang et al., 2019).

CO_2-induced wellbore cement degradation is an important process that governs the potential for CO_2 leakage along wellbores. (Xiao et al. 2017) developed a continuum-scale reactive transport model to analyze the process of CO_2 leakage through the interface between wellbore cement and the surrounding caprock. Unlike other studies that only consider CO_2-water-rock reactions, (Xiao et al. 2017) considers the combined geochemical reactions of CO_2 with cement and the caprock. Their simulation results showed a steady increase of $CaCO_3$ volume fraction at the cement-caprock interface, which reduced the risk of CO_2 leakage through the interface. Simulated calcium-silicate-hydrate (CSH) degradation in cement was limited, suggesting that a wellbore could maintain its integrity and structure under the considered conditions.

If CO_2 leakage along a wellbore does occur, the leaked CO_2 can enter shallow aquifers and possibly cause contaminant release. Continuum-scale reactive transport models were used developed a continuum-scale reactive transport model to study heavy metal release at the shallow aquifer due to CO_2 and brine leakage into the

shallow aquifer (Zheng and Spycher 2018), and the effect of clay minerals on CO_2-induced contaminant release (Viswanathan et al. 2012). These studies found that the release of heavy metals in shallow aquifers is primarily due to carbonic acid-driven mobilization of adsorbed and exchangeable metals in shallow aquifer sediments, and the reversible sorption of heavy metals to clay minerals through surface complexation are the key reactions in governing heavy metal concentrations in shallow aquifers.

In summary, the key geochemical processes in geologic CO_2 storage include the reaction between host rock and CO_2, the reaction between caprock and CO_2, the reaction between wellbore cement and CO_2, CO_2 leakage along wellbores with reactions, and CO_2-induced contaminant release to shallow aquifers, etc. (Figure 5). All of these key geochemical processes can be well simulated by reactive transport modeling.

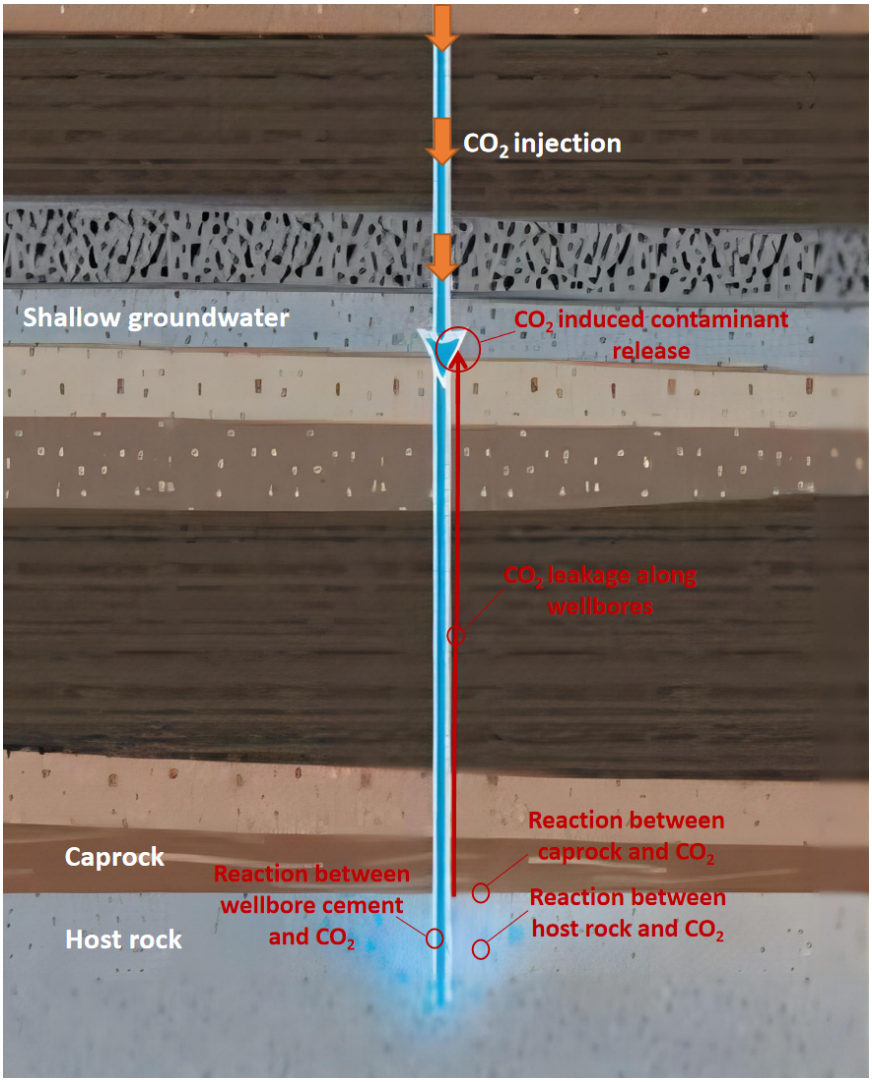

Figure 5: A schematic showing the key geochemical processes in geologic CO_2 storage that can be simulated by reservoir-scale reactive transport modeling

4.2 Environmental remediation applications

Continuum scale reactive transport model has been regarded as a powerful tool to study field-scale environmental remediation processes. A wide range of models have been used to describe the bioremediation of groundwater contaminants (Thullner and Schäfer 1999; Schäfer 2001; Barry et al. 2002; Brun et al. 2002; Herold et al. 2011; Verardo, Atteia, and Prommer 2017) but also processes like removal of contaminants from groundwater by precipitation, microbially induced carbonate precipitation (MICP) for soil strengthening, etc. For example, (Li Li et al. 2010) developed a continuum scale reactive transport model to investigate the spatial distributions of mineral precipitates and biomass accumulated during a biostimulation field experiment for dissolved

uranium removal. The model predicted that the uranium in the dissolved phase was converted into solid uraninite and was removed from groundwater, suggesting a promising uranium bioremediation efficacy. (Minto, Lunn, and El Mountassir 2019) presented a continuum scale reactive transport model to simulate the process of MICP for soil strengthening, erosion control, well leakage mitigation, and trapping of contaminants. Their model was able to capture the key processes of bacteria transport and attachment, urea hydrolysis, tractable $CaCO_3$ precipitation, and modification to the porous media in terms of porosity and permeability. Their simulation results successfully captured the distribution of microbially induced $CaCO_3$ around the 8 injection wells and showed a variation of $CaCO_3$ precipitation pattern given different flow injection rates.

4.3 Geothermal applications

Continuum scale reactive transport model has also been applied to predict geothermal fluid migration in geothermal fields. The high temperature in geothermal fields usually induces very fast mineral dissolution and precipitation, which then affects fluid migration. For example, (Hou et al. 2019) found that precipitation-induced sealing processes occurred in the fault-controlled geothermal system in the Guide Basin, China. (Alt-Epping et al. 2013) studied the impact of CO_2 exsolution on production well scaling at Bad Blumau geothermal field, Austria, which showed a fast precipitation of carbonate minerals in the production well without chemical inhibitors. In addition to carbonate minerals, SiO_2 phases (SiO_2(am), quartz and moganite) are important contributors to the clogging of geothermal fluid migration paths, which was demonstrated by reactive transport model results of a geothermal field in Iceland (Aradóttir et al. 2012). Their results are consistent with other simulation results and experimental observations, which show that CO_2-induced plagioclase dissolution releases H_4SiO_4 (aq), and a supersaturation state of H_4SiO_4 (aq) causes precipitation of SiO_2 phases (L. Zhang et al. 2015; Soong et al. 2018).

4.4 Earth's critical zone

An emerging area of application for the continuum scale reactive transport modeling is the research of Earth's critical zone. Earth's Critical Zone is the thin surface layer of the Earth that extends from the top of the vegetation to the bottom of drinking water aquifers. Earth's Critical Zone provides important environmental goods and services that are essential for humanity, and the physical, geochemical and biological processes are extremely complicated in Earth's Critical Zone. Continuum-scale reactive transport model provides an important tool to dissect the relationship between water chemistry and hydrological cycles, to track biogeochemical cycling driven by surface-subsurface water exchanges and in response to climate changes (L. Li 2019; Beisman, Maxwell, and Navarre-Sitchler 2015; Li et al. 2017; Khurana et al. 2022a, [b] 2022). Continuum-scale simulations for Earth's Critical Zone usually involve two-phase (water + air) flow simulation and partitioning of chemicals between water and

air, and an accurate determination of relevant parameters like relative permeability curves and partitioning coefficients of chemical compounds are the key to ensure the validity of the continuum-scale reactive transport model.

5. Discussion

It is important to acknowledge that each of the modeling approaches discussed are faced with limitations. Pore scale models are known for their high computational intensity and small computational domains that raise questions about representativeness and generality of the results. Pore network models can save computational cost but may sacrifice accuracy and predictive capacity, due to the simplifications of individual pore geometries and governing equations. The micro-continuum scale models have expanded the capability of pore (network) scale models by integrating continuum scale theories and enabling considerations of pore-scale chemical-physical heterogeneity. They are particularly useful in the presence of large contrast of pore size distribution where the larger pore are resolved while the smaller pores are modeled (e.g. fractured media, sub-voxel porosity in micro-CT images). However, they may face similar computational constraints as the pore-scale model do because pore-scale governing equations are solved. Even with continuum-scale models, the computational cost can be an issue if a complex reaction network requires the simulation of a large number of reactions and reactive species and when local heterogeneities need to be refined, and a balance between mesh resolution and area of investigation is required. The most notable challenge of the continuum-scale models is the wide use of constitutive relations that are yet to be validated and improved, in order to capture the nonlinearity that can arise from the geochemical dynamics and its interplay with other processes and relax the dependence on case-specific parameter calibration.

It is conceivable that combining more than one of these approaches may help address some of the challenges while retaining certain advantages, and thus necessary when used in practical applications (Blunt et al. 2013; Scheibe et al. 2015). There are three common practices. One approach is the hybrid method in which different models are used in different sub-domains, and conservations are checked at the boundary to ensure consistency of flow and transport (Molins et al. 2019). It can save computational costs associated with having to solve the pore scale equations in the entire domain, but the communication time between different domains through boundary conditions can be considerable. The second approach involves modeling the same domain using different models, and thus requires communication both ways via boundary conditions or averaged properties. For example, (Gärttner et al. 2020)developed a micro-macro model for mineral dissolution that solves pore-scale equations in the auxiliary cells, which supply averaged coefficient functions to the macro-scale model of the corresponding porous domain. The third approach that can be much more computationally efficient and generalizable involves mathematical homogenization of the pore-scale equations and calibration of the effective parameters using micro-macro relationships, e.g., by developing improved constitutive relations for coarser models using models at refined scales (Hang Deng et al. 2018).

One important consideration when passing information across scales or performing upscaling is that certain properties have different meanings at different scales, and the

microscopic parameter may not have a one-to-one mapping to the ‘corresponding’ macroscopic parameter. This issue is particularly evident in parameters that describe geochemical dynamics. Parameters such as reaction rate and accessible reactive surface area are used at both pore and continuum scales.In the case of reaction rate, the continuum scale values can be orders of magnitude lower, which may be caused by the mineralogical heterogeneity at the finer scales or by the chemical gradients created by flow and transport processes (Maher et al. 2006). Similarly, accessible reactive surface area at the continuum scale may differ from geometric surface area that is easier to quantify, which introduces ambiguity in its parameterization (Lauren E. Beckingham et al. 2017). The lack of consistency in the physical meanings and measurements of variables at different scales goes along with the empirical nature of their continuum scale descriptions. It highlights that when coupled processes are involved, upscaling of these processes needs to be coordinated to accurately reflect the coupling of these processes at the finer scales. While pore-scale models can provide fundamental understanding of the coupling at the finer scales, representing it in a mechanistic manner is key to improve the predictive capability of coarser scale models, and is still challenging. Moreover, the continuum-scale properties (e.g., surface area, diffusivity, and permeability) evolve with pore structures that can be altered by reactions such as mineral dissolution and precipitation, and are typically approximated by a function of parameters such as porosity. Whether such constitutive relations or the upscaling strategies hold throughout the dynamic evolution and whether they are independent of the trajectory of system evolution are questions that need to be addressed.

For fully coupled multiphysics (e.g., chemical, hydrological, mechanical, thermal, biological) problems, improving modeling efficiency is a major challenge, and one important consideration is the time stepping given the presence of multiple time scales. To ensure convergence, time stepping (commonly constrained by courant number) is typically controlled by the process with the smallest characteristic time scale. It may be unrealistic and unnecessary to update other processes with larger characteristic time scales using the same time step. In these cases, it is common to assume a quasi-steady state and update those processes at a coarser time step. This can save a lot of computational cost especially when processes solved at the coarser time step are computationally intensive. However, to prevent large error buildup when processes requiring small time steps are involved, it is necessary to use small tolerance values, especially for mass conservations, which may also result in large computational time as the number of iterations may be increased. In complex geochemical systems, a single time step for geochemical calculation may not be able to accurately describe all geochemical processes. In addition to numerical considerations, ensuring the feedback between processes throughout system evolution is properly captured by the choice of time steps is also critical. For example, in presence of mineral precipitation, overshoot - i.e., a large amount of local precipitation that exceeds the available pore volume in the grid - may occur which can cause the simulations to fail and is unphysical.

Overall, to address the multiphysics and multi-scale challenges faced by many practical geochemical systems, smart modeling capability is needed, to be able to optimize local and global selection of the appropriate modeling approach, mesh resolution and time stepping. Meanwhile, machine learning algorithms have been increasingly used to bypass explicit description of (some of) these coupled processes (Mudunuru and Karra 2021; Sprocati and Rolle 2021; Prasianakis et al. 2020; Leal et al. 2020). While great potential has been recognized

regarding the application of machine learning, especially with the advances in physics-informed algorithms, it is crucial to ensure continuous development of high-fidelity process-based models (D'Elia et al. 2022). Recent development of characterization and experimental techniques have provided a lot of data to support the development and validation of models. However, benchmark problems that allow cross-comparisons of different models and thus build confidence in the community are yet to be enriched. One important trend of development of multiphysics models is the use of application program interfaces (e.g., alquimia in (P. Li, Deng, and Molins 2022; Beisman, Maxwell, and Navarre-Sitchler 2015)), but this calls for the sharing of well-validated codes. There are quite a number of publicly available repositories, modeling and simulation packages that can be of great value to researchers (C. I. Steefel et al. 2015). These include open source software, collections of 3D micro-CT images and the related publications. In the following table, we summarize some codes that are referenced in this perspective paper.

Table 1. Summary of reactive transport codes at various scales

Code name	Capability Description	Reference
MIN3P	a general purpose multicomponent flow and reactive transport code for variably saturated media providing a high degree of flexibility with respect to the definition of the reaction network.	(Mayer, Frind, and Blowes 2002; Sihota and Ulrich Mayer 2012)
CrunchTope based model	Open access reactive transport code for single phase continuum-scale reactive transport modeling	(C. I. Steefel et al. 2015)
	CrunchFoam: pore scale reactive transport modeling platform building on OpenFOAM and CrunchTope using Alquimia	(P. Li, Deng, and Molins 2022) For OpenFOAM (Weller et al. 1998)
	Crunch-Comsol: micro-continuum scale reactive transport modeling platform building on CrunchTope and COMSOL multiphysics	(Q. Zhang et al., n.d.)
TOUGH family codes	A family of codes for multiphase flow simulations and reactive transport modeling in fractured porous media at the continuum scale/reservoir scale.	(Xu et al. 2008)OL.9
Pflotran	Open access software package for reactive transport modeling in multiphase systems at the continuum scale/reservoir scale.	(Hammond, Lichtner, and Mills 2014)
mgstat	a MATLAB toolbox that gives an interface to some geo-statistical open source toolkits such as GSTAT, VISIM and SGeMS	(Hansen 2004)

OpenPNM	an open-source pore network modeling package, written in Python. It includes built-in transport algorithms but can be fully customized	(Gostick et al. 2016)
porousMedia4Foam	Open access reactive transport platform building on OpenFOAM and PhreeqC using a micro-continuum approach	(Soulaine et al. 2021)
geochemFoam	Open access pore scale reactive transport modeling platform building on OpenFOAM and PhreeqC	(Maes and Menke 2021)
OpenGeoSys	an open source software for the development of numerical methods for the simulation of thermo-hydro-mechanical-chemical (THMC) processes in porous media	(Kolditz et al. 2012)
	For reactive transport applications the code is also coupled to reactive modules like PhreeqC or BRNS.	(Centler et al. 2010; He et al. 2015)
PNBRNS	a MATLAB-based 2D reactive model that solves biodegradation of reactive compounds in regular pore-networks.	(Gharasoo et al. 2012, 2014)
SGeMS	an open source geo-statistical package including most recent multiple-point statistics implementations	(Remy 2005)
STOMP	Subsurface Transport Over Multiple Phases, a numerical simulator for coupled processes in the subsurface developed by Pacific Northwest National Laboratory	(S. K. White et al. 2020)
MOOSE	Multiphysics Object Oriented Simulation Environment, an open source parallel finite element modeling framework developed for coupled processes including geochemistry by Idaho National Laboratory	(Permann et al. 2020)

6 Conclusion

In this perspective paper, we provide an overview of recent development of pore-scale, pore network scale, micro-continuum scale, and continuum scale models for coupled geochemical-physical processes in porous media, in the context of practical applications including geologic carbon storage, environmental remediation, and (un)conventional oil/gas recovery, etc. Advances in these modeling capabilities have enabled improved understanding of pore-scale dynamics and the impacts of pore-scale mineralogical and morphological

heterogeneity on porous media evolution, and better predictions of reservoir scale dynamics. However, modeling challenges remain for capturing the intricate coupling of multiple processes across spatial and temporal scales efficiently. Future studies are needed to develop smart modeling capability and to enable cross-model comparisons.

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