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Characterisation of reactive transport in pore-scale correlated porous media

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HIGHLIGHTS

- Effect of correlation length on reactive transport is quantified.
- Unstructured irregular pore spaces with different correlation lengths are generated.
- Conceptual diagrams are suggested to characterise reactive transport in porous media.

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ABSTRACT

We apply a reactive transport model to study the effect of correlation length on dissolution and to characterise reactive transport in pore-scale correlated porous media. Porous media with different correlation lengths are derived from correlated fields. An efficient numerical model is employed to simulate dissolution on these geometries for a range of Péclet and Damköhler numbers. The solute concentration distribution is presented in porous media for both low and high correlation lengths. Four types of dissolution patterns are observed in various correlated porous media: face dissolution, uniform dissolution, wormholing and mixed dissolution. The permeability-porosity relationships are also studied in simulations of porous media with different correlation lengths. The permeability in larger correlation length media increases faster at the same Damköhler number. Dissolution patterns of all cases are plotted in a diagram and the effect of correlation length on reaction regimes are analysed. The findings show that larger correlation lengths can result in more uniform and wormholing types of dissolution but less face dissolution. Correlation length plays a critical role in characterising the reaction regimes during reactive transport.

1. Introduction

Reactive transport in porous media is of importance in many applications, including catalyst optimisation in chemical engineering (Keil and Rieckmann, 1994), carbon dioxide capture and storage (Blunt et al., 2013), environmental contaminant remediation (Nick et al., 2013) and enhanced petroleum recovery (Daccord et al., 1989). In the sequestration of carbon dioxide in carbonate reservoirs, geochemical reactions involving CO_2, brine and carbonate occur in the flow paths of geological media. These reaction processes generate an acidic solution dissolving the host rocks and affecting the safety of long-term storage (Menke et al., 2015). Besides, for solving contamination problems related to underground water, biological or chemical reactors are used to remove hazardous pollutants. When contaminated water flows through these reactors (Rieckmann and Keil, 1997), chemical reactions take place reducing the contaminant concentration. Additionally, acid injection into the geological formation around wellbores is often applied to reduce skin effects to improve fluid flow and enhance hydrocarbon recovery from reservoir rocks (Daccord et al., 1989; Fredd and Fogler, 1999).

Transport in porous media is characterised by Péclet (*Pe*) number, which is defined as the ratio of advection to molecular diffusion. Damköhler (*Da*) number describes the strength of reaction over molecular diffusion. A range of numerical methods have been derived to explore flow and reaction in porous media (Blunt et al., 2013; Gerami et al., 2016; Mostaghimi et al., 2017, 2015; Tartakovsky et al., 2007). Bekri et al. (1995) used random walks and finite difference methods to investigate the effect of convection, diffusion and chemical reactions on dissolution patterns in porous media with various geometries. They observed uniform dissolution and "wormholing" in their dissolution studies and found

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that the dissolution patterns are determined by *Pe* and *PeDa*. Algive et al. (2007) applied pore network models to study the effect of reaction regimes on permeability and porosity relationships and compared their results with experiments in glass micromodels. They changed the values of *Pe* and *PeDa* to obtain different reaction regimes and found that permeability and reaction patterns are scale dependent. Varloteaux et al. (2013) used pore network modelling to investigate the evolution of petrophysical properties due to reaction. They showed that the relationship of permeability and porosity depends on the reaction patterns characterised by *Pe* and *PeDa*. Kang et al. (2014) applied a reactive transport model based on the lattice Boltzmann method to study the variations of permeability and porosity induced by dissolution. Their results show that the permeability-porosity relationships during dissolution are not only characterised by Péclet and Damköhler but also dependent on the complexity of porous media structures. However, they did not quantify the effect of porous media structure.

Apart from Péclet and Damköhler numbers, recent studies have shown that the reaction regimes and petrophysical variations in reactive flow are related to the pore structures (Alhashmi et al., 2016; Kang et al., 2014; Liu and Mostaghimi, 2017c; Pereira Nunes et al., 2016). Mostaghimi et al. (2016) applied lattice Boltzmann and finite volume methods to simulate reactive flow on micro-CT images of rocks with different levels of heterogeneity. They found the permeability variation due to reaction is influenced by pore scale heterogeneity. The more heterogeneous the pore structure is, the faster the permeability increases during dissolution. Pereira Nunes et al. (2016) used a particle-based method to study the impact of pore structure on average reaction rates in three types of rocks. Reaction simulations were performed in different flow regimes and their results showed that the average reaction rate is dependent on pore-scale heterogeneity and advection rates.

However, most descriptions of pore-scale heterogeneity in direct simulations on micro-CT images are based on the analysis of velocity distribution or tortuosity (Alhashmi et al., 2016; Mostaghimi et al., 2016; Pereira Nunes et al., 2016). Geometrical properties used in pore network modelling like coordination number, pore size distribution (Joekar-Niasar et al., 2013; Joekar Niasar et al., 2009) have not been analysed systematically for reactive transport. The correlations between pore space heterogeneity and reaction regimes have not yet been quantitatively illustrated in direct simulation of reactive transport. A geometrical description should be introduced to characterise pore structure and link it to the reaction processes.

Correlation lengths describe the spatial correlations between the pore spaces in porous media, which has been used to provide quantitative analysis of correlated pore scale heterogeneity (Babaei and Joekar-Niasar, 2016; Bijeljic et al., 2013; Knackstedt et al., 1998, 2001). In porous media, the correlation length λ represents some average distance between any two sites belonging to the same cluster of the pore space (Stauffer and Aharony, 1994). The correlation length is an important parameter for measuring the percolation characteristics and conductivity of porous media (Hunt, 2001). The calculation of electrical conductivity is also dependent on the correlation length and porosity of porous media (Ioannidis et al., 1997). The significance of correlation length in fluid flow and petrophysical properties has been illustrated in many studies. Knackstedt et al. (2001) incorporated correlation length into pore network models to describe the correlated heterogeneity and study its significance in two phase flow. They compared the numerical results with experiments and found that the correlations between pore spaces have great impact on fluid distribution in porous media. Leng (2013) applied a dynamic pore network model to study the impact of spatial correlation on viscous fingering in geological formation. They simulated fluid flow in different pore networks with varying correlation lengths and showed that larger correlation lengths yield more significant viscous fingering effect. Babaei and Joekar-Niasar (2016) used pore network modelling to investigate the effect of correlation length on transport regimes. They performed simulations of dispersion in porous media with various correlation lengths for different Péclet numbers. The results showed that with increase of correlation length, the range of mixed advection-dispersion regime becomes narrower and the impact of Péclet numbers on transition regime reduces.

It is of interest to quantify the pore space geometry with correlation length and characterise reaction in porous media, which can provide systematical applications for different types of porous media. Once this relationship is established, desirable reaction results can be quantitatively predicted and reproduced. Herein, we aim to present a reaction characterisation diagram to relate the reactive transport with the correlation length. We generate unstructured irregular pore spaces with different correlation lengths and simulate reactive transport in regimes of various Péclet and Damköhler numbers and classify the reactive transport types.

2. Pore structure generation

The correlation length for porous media is usually described by the empirical semi-variogram. For a given property, such as porosity φ, it is defined as

$$\gamma_{\varphi}(h) = \frac{1}{2N(h)} \sum_{i=1}^{N(h)} [\varphi(z_{i+h}) - \varphi(z_h)], \tag{1}$$

where $\gamma_{\varphi}(h)$ is the semi-variogram, h is the distance between two data points, $N(h)$ is the number of data points and z is the location of data. Dissimilarity between two separate data points with a distance of h is measured. When a plateau is reached in the variogram, the data is uncorrelated. To investigate the effect of correlation length on reactive transport, pore geometries with different correlation lengths (λ) are generated. We use the method developed by Cirpka and Attinger (2003) to generate correlated fields. An isotropic model is applied in the generation of correlated fields and thus the geometrical properties are similar for all the geometries. The only difference between all the pore geometries is the correlation length. The geometry generation is performed in three steps:

Step 1: We generate the correlated fields with the field generator developed by Cirpka and Attinger (2003). This generator utilises the Fourier transform of the covariance function to obtain the spectral density function in a random autocorrelated field. The created fields are periodic due to the application of discrete Fourier transformation in this method. We use an isotropic Gaussian variogram, $\gamma(h) = \sigma_Y^2 \exp\left(-\frac{\pi h^T h}{4\lambda^2}\right)$, for a second-order stationary field of $Y = \ln R$ where $\gamma(h)$ is the auto-covariance of the log conductivity fluctuations with lag distance interval h, R is the uniform geometric mean of the hydraulic conductivity and λ is the correlation length. We include the mean of Y (indicated by μ_Y) into the fast Fourier transform of the random correlated field. The mean and variance of R (σ_Y^2 and μ_Y) is expressed as:

$$\mu_Y = \ln\left(\frac{\mu_R^2}{\sqrt{\sigma_R^2 + \mu_R^2}}\right) \tag{2}$$

$$\sigma_Y^2 = \sqrt{\ln\left(\frac{\sigma_R^2}{\mu_R^2} + 1\right)} \tag{3}$$

Step 2: To derive the porous geometry, segmentation is carried out by applying the simplest and most commonly used method of segmentation. A threshold value *th* is given to distinguish the pore