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Pore-scale numerical investigation of the impacts of surface roughness: Upscaling of reaction rates in rough fractures

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Abstract

The roughness of solid surfaces influences mineral dissolution rates by affecting flow and transport in the near-surface regions and by increasing the surface area available for reaction. The impact of surface area is commonly accounted for by using the surface roughness factor (SRF), which is the ratio between the total surface area and the nominal or geometric surface area. The coupled impacts of hydrodynamics and transport, however, are rarely considered. In this study, we performed pore-scale reactive transport simulations in a series of synthetic 2D rough fractures to investigate the compound effects of surface roughness on the reaction rates in fractures. Simulation results show that while reaction rates increase with SRF, the increase is not linearly proportional to that of the surface area. Rather, local concentration gradients resulting from flow and transport processes limit the increase in the rate. In addition, surface roughness gives rise to concentration gradients that do not otherwise develop in the flat-surface geometries typically considered in modeling studies. To describe the impacts of the surface area increase on reaction rate at different roughness and flow velocities, three distinct regimes were identified. A unified mathematical relationship was also developed that allows the reaction rate in a rough fracture to be approximated by the well-mixed reactor reaction rate and a correction factor. The correction factor follows a power-law function of SRF, with the multiplying factor and exponent expressed as exponential functions of the Péclet and Damköhler number. This mathematical formulation provides a valuable upscaling approach for effective integration of sub-grid scale surface roughness in larger scale continuum models.

Keywords: Surface roughness; Reaction rate; Upscaling; Fracture; Pore-scale reactive transport model

1. INTRODUCTION

Reaction rates measured in the lab are typically orders of magnitude higher than those observed in the field. This discrepancy has been attributed to two types of factors: intrinsic and extrinsic (White and Brantley, 2003; Liu et al., 2015). The intrinsic factors include the density and diversity of reactive sites (Gautier et al., 2001; Maher et al., 2006; Fischer et al., 2014), while extrinsic factors include hydrological and microbial processes (Maher, 2010; Wen and Li, 2017). For example, the residence time in the field is typically longer and the reactions are close to equilibrium compared to lab experiments (Maher, 2010). Passivation due to the development of a weathered layer or secondary precipitation observed in the field may have also contributed to the lower reaction rate (Noiriel et al., 2007; Maher et al., 2009; Navarre-Sitchler et al., 2011). Some investigators have suggested that the scale dependence of reaction rates contributes to this discrepancy (Li et al., 2008). Given the dependence of reaction rates on scales, a fractal description was proposed to predict the reaction rate of basalt weathering at a given length scale

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from BET scale reaction rate (Navarre-Sitchler and Brantley, 2007). Overall, this scale dependence is a manifestation of concentration gradients resulting from heterogeneity of flow, transport and reactions operating at the fine scale. This observation also highlights the challenge for large-scale modeling, in which homogenization of fine scale heterogeneity is a common practice. Therefore, mechanistic understanding of how fine scale heterogeneity affects large scale processes and properties is needed for the resolution of scientific conundrums such as the scale dependence of reaction rates, and for the development of modeling approaches that allow effective upscaling of fine-scale heterogeneity.

One type of heterogeneity that is of general interest and is the focus of this study is surface roughness. Surface roughness affects the reactivity of the solid phase by increasing surface area. As shown in the commonly used reaction rate laws, reactivity of the solid phase is typically treated as linearly proportional to the physical surface area. Quantification of surface roughness, however, is challenging because of the scale dependence of surface measurements and the large number of metrics that have been used to define surface roughness in different disciplines, including height difference, root mean square roughness, joint roughness coefficient, surface roughness factor, and fractal dimension and amplitudes (Fischer and Luttge, 2007; Bandstra and Brantley, 2015). The selection of surface roughness measurement should be guided by the nature of the studies. Traditionally in geochemistry, a surface roughness factor (SRF) is used to account for the impacts of surface roughness on reaction rates (Fletcher and Brantley, 2010; Beckingham et al., 2016). SRF is defined as the ratio between the total surface area, which is typically determined by the Brunauer-Emmett-Teller method, and the geometric surface area, which can be estimated based on ideal geometry or computed tomography images (Peters, 2009; Lai et al., 2015).

Surface roughness can also influence the reaction rate by affecting flow and transport. For example, surface roughness can increase the hydraulic tortuosity in the fracture flow and result in fracture permeability decrease (Deng et al., 2013; Jin et al., 2017). The effective permeability has been reported to have a power law dependence on the mean fracture aperture, and the exponent of the power law relationship is determined by surface roughness that is characterized by the Hurst exponent (Jin et al., 2017). It has also been observed that compared to a smooth fracture of the same average aperture, surface roughness leads to an earlier breakthrough of a conservative solute and a longer tailing. The early breakthrough is ascribed to higher velocity in the middle of the rough fracture, whereas the long tailing is a result of the development of the relatively immobile zones in the roughness (Bolster et al., 2009, 2014; Cardenas et al., 2009; Bouquain et al., 2012; Chaudhary et al., 2013; Sund et al., 2015). Consequently, the dispersivity coefficients are functions of not only the Péclet number, but also the fracture geometry and the Reynolds number (Bouquain et al., 2012; Richmond et al., 2013). Péclet number measures the relative magnitude of advection and diffusion, and is defined by the average velocity ($\bar{u}$), the average aperture (b), and the molecular diffusion coefficient (D_m).

$$Pe = \bar{u}\,b/D_m \tag{1}$$

Reynolds number is the ratio between the inertial force and the viscous force,

$$Re = \bar{u}\,L/\nu \tag{2}$$

where L and ν are the fracture length and the kinematic viscosity of the fluid, respectively.

Accounting for the impacts of surface roughness on reaction rates over a rough surface is challenging not only because roughness affects reaction rate through surface area, hydrodynamics and transport, but also because solid phase reactivity, hydrodynamics and transport are intimately coupled. As such, a scaling factor, in addition to the surface roughness factor, has typically been used to correct surface area for mineral accessibility or transport limitation (Moore et al., 2012; Beckingham et al., 2017). The determination of the scaling factor, however, is arbitrary and is often a calibration exercise rather than having a physical basis. Few studies have investigated the interplay between flow, transport and reaction in rough fractures or pores and the subsequent impacts on mass transfer of a reacting solute or bulk reaction rate. These studies further highlighted the need to account for the compound effects of surface roughness on reaction rates in a rough fracture or pore. Jeschke and Dreybrodt (2002) investigated the extent to which surface area associated with micro-pores and complex surface morphology contributes to reactions under conditions commonly used for experimental determination of mineral reaction rates. Using a linear reaction rate, the authors developed analytical solutions for the transport equation in presence of a diffusion boundary layer. While the solutions allow quantification of the contribution of surface area of open pores to reactions, they do not account for the development and dynamic change of the diffusive boundary layer as a result of surface morphology, reaction and flow. Dykaar and Kitanidis (1996) studied the relationship between the micro-scale and macro-scale reaction and transport properties for a reacting solute that is being consumed at a linear rate in a porous medium, which was represented by a sinusoidal structure. Their numerical results showed that the relationship varies with the Péclet and Damköhler number (which measures the relative magnitude between the time scales of flow or transport and reaction) of the system. Sund et al. (2015) investigated the transport of a reacting solute through a rough channel and demonstrated that an upscaled random walk model can be used to capture the breakthrough curve of the reacting solute. Cvetkovic and Gotovac (2014) upscaled chemical transport in fracture networks using a time domain random walk approach by incorporating heterogeneity of the flow in the effective surface area. These studies, however, focus on linear reaction systems, and it has been suggested that further investigations are needed for nonlinear reactions (Sund et al., 2015).

Therefore, there is a research need to evaluate and quantify the compound effects of surface roughness on nonlinear water-rock reactions. The objectives of our study are to