



An upscaled rate law for mineral dissolution in heterogeneous media: The role of time and length scales

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Abstract

An upscaled rate law is developed for mineral dissolution in heterogeneous media under variable residence time (flow velocity) and length scale conditions, expanding the previous rate law under one flow and length condition (Wen and Li, 2017). A total of 640 Monte-Carlo numerical experiments were carried out with magnesite dissolution within quartz matrix in spatially heterogeneous media characterized by permeability variance ($\sigma_{\text{mk}}^2 = 6.0$) and correlation length ($\lambda = 2\text{--}50$ cm) under a range of domain length (1.0–5.0 m) and flow velocity (2.7×10^{-4} to 27.0 m/day) conditions. The upscaled rate law $R_{ht} = kA_T \left[1 - \exp\left(-\frac{\tau_{eq}}{\tau_a}\right)\right] \left\{1 - \exp\left[-L\left(\frac{\tau_a}{\tau_{ad,r}}\right)\right]\right\}^\alpha$ consists of two parts. The first is the rate law in equivalent homogeneous media $R_{hm} = kA_T \left[1 - \exp\left(-\frac{\tau_{eq}}{\tau_a}\right)\right]$, where rates depend on rate constants (k), total mineral surface area (A_T), and the relative timescales of reactions (τ_{eq}) and advection (τ_a) ($Da = \frac{\tau_a}{\tau_{eq}}$). The second term $\chi = \left\{1 - \exp\left[-L\left(\frac{\tau_a}{\tau_{ad,r}}\right)\right]\right\}^\alpha$ is the heterogeneity factor that quantifies the deviation of heterogeneous systems from their homogeneous counterparts. The term includes the relative transport time ratio $\frac{\tau_a}{\tau_{ad,r}}$, domain length (L), and geostatistical characteristics of spatial heterogeneity (permeability variance in $\alpha = \frac{5}{\sigma_{\text{mk}}^2}$). The ratio $\frac{\tau_a}{\tau_{ad,r}}$ quantifies the relative timescales of transport at the domain scale (τ_a approximates τ_{ad}) versus transport in the reactive zones ($\tau_{ad,r}$). Under low flow velocity and/or long domain length conditions where $\tau_a > \tau_{ad,r}$, homogenization occurs so that χ is close to 1 and heterogeneity effects are negligible. In contrast, χ deviates from 1 by up to 2 orders of magnitude under short length and fast flow conditions where $\tau_a < \tau_{ad,r}$ and $L\left(\frac{\tau_a}{\tau_{ad,r}}\right)$ is small. Under such conditions, transport rates in and out of the reactive zones limits the overall dissolution at the domain scale. The rate law predicts that 1) heterogeneity effects are governed by the relative magnitude of mineral-water contact in reactive zones versus in the whole domain; 2) dissolution rates in heterogeneous media ultimately approach asymptotic values in homogeneous media at “sufficiently” long lengths. It takes longer distance (and time) for more heterogeneous systems with longer $\tau_{ad,r}$ values to reach the asymptotic values. This is supported by carbonate dissolution rates calculated from river water chemistry data. Although the rate law is derived based on magnesite dissolution, it is expected to be applicable for the dissolution of other minerals, as long as the dissolution characteristics of other minerals (e.g., k , A_T , and K_{eq}) are incorporated in the rate law.

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1. INTRODUCTION

Mineral dissolution is important in regulating atmospheric CO₂ levels, water chemistry, soil formation, biogeochemical cycles, among others. Extensive studies have

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documented mineral dissolution rates measured in natural subsurface systems that are 3–6 orders of magnitude lower than those measured in well-mixed batch reactors (Paces, 1983; White and Brantley, 2003; Navarre-Sitchler and Brantley, 2007). This discrepancy has been attributed to intrinsic factors including reaction affinity, secondary mineral precipitation, and surface roughness (Zhu et al., 2010; Putnis, 2014; Beckingham et al., 2016), as well as extrinsic factors including water saturation, flow conditions, temperature, and microbial activities (Bonneville et al., 2011; Molins et al., 2012; Hattanji et al., 2014; Li et al., 2016).

In the natural subsurface, water operates as a reactant and a transport agent of mineral dissolution. Export of dissolved products by advective transport and fast replenishment of fresh water drives reactions by maintaining their distance from thermodynamic equilibrium. Water residence times, the contact times between water and minerals, therefore regulate the extent of disequilibrium and dissolution rates (Lichtner, 1993; White et al., 2001; Maher, 2010). Short fluid residence time leads to rapid transport compared to mineral-water surface kinetics so that overall reaction rates (mass/time) are controlled by surface reaction kinetics (kinetic-controlled) (White et al., 2001). On the other hand, long residence times mean slow advective transport compared to surface reaction kinetics so that reaction rates are transport controlled (Berner, 1978; Navarre-Sitchler et al., 2011). The overall dissolution rates are an outcome of coupling between reaction and transport. Such coupling is often quantified by the relative timescales of reactions (to reach equilibrium) versus transport (advection and diffusion/dispersion) through dimensionless numbers including Péclet number (time scales of diffusion/dispersion versus advection) and Damköhler number (time scales of transport versus reaction) (Salehikhoo et al., 2013; Maher and Chamberlain, 2014).

Spatial heterogeneities, i.e., the spatial variation in mineral texture and properties, exist ubiquitously in natural subsurface systems. Large spatial variations in permeability lead to the formation of preferential flow paths and “anomalous” (or non-Fickian) early arrivals and long tails (Dagan, 1984; Le Borgne et al., 2010; Heidari and Li, 2014). This means timescales of advective transport can be highly variable (Rajaram, 1997; Dentz et al., 2004) and average fluid residence time may not reflect the contact time between water and minerals of differing reactivity in heterogeneous media. That is, the time that water interacts with reactive minerals may vary by orders of magnitude (Wen and Li, 2017). Extreme examples are fractured rocks or karstified formations, where fluid primarily flushes through highly conductive conduits with very short residence times so that mineral dissolution mostly occurs at the rock-fracture interfaces with residence times that are orders of magnitude higher (Hartmann et al., 2014; Cao et al., 2015; Brunet et al., 2016; Wen et al., 2016). The concept of exposure time has been proposed to quantify the contact time between water and reacting minerals, in an effort to distinguish from the mean fluid residence time (Ginn, 1999; Sanz-Prat et al., 2016).

Decades of literature have shown that effects of spatial heterogeneity on solute transport are temporal and spatial

scale dependent. Long residence times (slow flow velocity or long spatial length) lead to short breakthrough tails of conservative tracers due to the transition from advective-dominating to diffusive-dominating transport in low permeability zones (Haggerty et al., 2000; Zinn et al., 2004; Heidari and Li, 2014), and therefore facilitate the transition from anomalous to Fickian transport even in highly heterogeneous media (Dentz et al., 2004; Meerschaert et al., 2008). Effective transport parameters, including hydraulic conductivity (Javaux and Vanclooster, 2006), connectivity (Renard and Allard, 2013), effective diffusivity (Zhang et al., 2006), and macrodispersivity (Gelhar et al., 1992), have been reported to be scale-dependent and reach their asymptotic limit when length scales are “sufficiently” long. For example, effective hydraulic conductivity has been found to increase with the scales of observation and approach approximately 1.0×10^{-3} m/s at 10 km (Schulze-Makuch et al., 1999). Effective matrix diffusion coefficients in fractured rocks increase by >3 orders of magnitude when the observation scales increase from 5.0 m to 2.0×10^3 m (Zhou et al., 2007). Longitudinal dispersivities in heterogeneous sandy aquifers have been documented to increase and reach an asymptotic value of approximately 1.0 m beyond 10^2 m (Gelhar et al., 1992), although recent work has questioned the possibilities of reaching asymptotic values (Zech et al., 2015).

The effects of spatial heterogeneities on multi-component geochemical reactions have been studied to a much lesser extent compared to conservative/sorptive solute transport (Rajaram, 1997; Li et al., 2007; Li et al., 2008; Deng et al., 2010; Pandey and Rajaram, 2016). For aqueous bimolecular reactions ($A + B \rightarrow C$), slow flow velocities have been shown to lead to fast decrease of reaction rates in highly heterogeneous porous media (Ederly et al., 2016). For single-component sorption, highly heterogeneous media limit sorption capacity while this dependence diminishes as domain length increases (Deng et al., 2010). The effects of heterogeneity for multi-component surface complexation have been found to largely depend on the connectivity of heterogeneous media (Wang and Li, 2015) and diminish at the domain scale of ~ 15 – 20 correlation lengths (Wang et al., 2018). The effects of spatial patterns on magnesite dissolution rates are significant under fast flow conditions and diminish under slow flow conditions as the systems approaching equilibrium (Salehikhoo and Li, 2015). Sanz-Prat et al. (2016) concluded that when transverse mixing is negligible, spatial variation in bioreactive chemical concentrations can be mapped using exposure time. In essence, as long as the contact time of reactants are the same, their resultant concentrations are the same no matter where they are. At large spatial scales such as watersheds, it is often not clear if variations in concentration and discharge data and chemical weathering rates are caused by spatial heterogeneities or other compounding factors such as differences in lithology, climate conditions, or length scales (Bluth and Kump, 1994; White and Blum, 1995).

Our previous work (Wen and Li, 2017) developed an upscaled rate law for magnesite dissolution in heterogeneous porous media under one flow velocity and domain length conditions. The rate law indicates that reactive resi-

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