



Evaluation of mineral reactive surface area estimates for prediction of reactivity of a multi-mineral sediment

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Abstract

Our limited understanding of mineral reactive surface area contributes to significant uncertainties in quantitative simulations of reactive chemical transport in subsurface processes. Continuum formulations for reactive transport typically use a number of different approximations for reactive surface area, including geometric, specific, and effective surface area. In this study, reactive surface area estimates are developed and evaluated for their ability to predict dissolution rates in a well-stirred flow-through reactor experiment using disaggregated samples from the Nagaoka pilot CO₂ injection site (Japan). The disaggregated samples are reacted with CO₂ acidified synthetic brine under conditions approximating the field conditions and the evolution of solute concentrations in the reactor effluent is tracked over time. The experiments, carried out in fluid-dominated conditions at a pH of 3.2 for 650 h, resulted in substantial dissolution of the sample and release of a disproportionately large fraction of the divalent cations. Traditional reactive surface area estimation methods, including an adjusted geometric surface area and a BET-based surface area, are compared to a newly developed image-based method. Continuum reactive transport modeling is used to determine which of the reactive surface area models provides the best match with the effluent chemistry from the well-stirred reactor. The modeling incorporates laboratory derived mineral dissolution rates reported in the literature and the initial modal mineralogy of the Nagaoka sediment was determined from scanning electron microscopy (SEM) characterization. The closest match with the observed steady-state effluent concentrations was obtained using specific surface area estimates from the image-based approach supplemented by literature-derived BET measurements. To capture the evolving effluent chemistry, particularly over the first 300 h of the experiment, it was also necessary to account for the grain size distribution in the sediment and the presence of a highly reactive volcanic glass phase that shows preferential cation leaching. © 2016 Elsevier Ltd. All rights reserved.

Keywords: Reactive surface area; CO₂ sequestration; Mineral reaction rates

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1. INTRODUCTION

Reactive transport modeling is a powerful approach for predicting the physical and chemical evolution of natural porous media systems (Steeffel et al., 2005). Accurate predictions, however, require a quantitative treatment of mineral dissolution and precipitation reactions. A good example is the problem of mineral trapping associated with subsurface CO₂ injection and sequestration (Gaus, 2010; Pham et al., 2011; Hellevang et al., 2013). The coupled dissolution and precipitation rates determine the time scales required for mineral trapping, but also modify the pore structure and pore- and pore-throat size distributions and connectivities (eg. Crandell et al., 2012). Rigorous modeling of these pore scale mineralogical processes is needed as they directly impact processes and parameters at larger scales, including permeability evolution (Beckingham et al., 2013; Noguees et al., 2013).

Mineral dissolution and precipitation reactions are typically slow in comparison to geologic CO₂ sequestration (GCS) injection time scales and the kinetics of these reactions need to be treated explicitly in quantitative numerical models for water–gas–rock interaction to predict long-term performance of the storage system. At present, the ability of continuum reactive transport models to accurately predict mineral reaction rates is limited (Black et al., 2015; Bourg et al., 2015), although there are some successes (Maher et al., 2009; Noiriél et al., 2012). One of the principal uncertainties in modeling mineral reaction rates comes from estimation of mineral reactive surface area rather than intrinsic rate values (Bourg et al., 2015; Wigley et al., 2013; Zhu and Lu, 2013). This limitation results in discrepancies in predicted pore structure evolutions (summarized in Gaus et al., 2008), amounts of secondary mineral precipitation (Hellevang and Aagaard, 2013; Bolourinejad et al., 2014), and the timescale of (trapping) reactions (Xu et al., 2014). Similar uncertainties are associated with the modeling of water–rock interaction processes in other environments, including marine diagenesis (Maher et al., 2006), chemical weathering (Maher et al., 2009; Navarre-Sitchler et al., 2011), contaminant fate and transport (Li et al., 2009), and geological nuclear waste repository performance (Marty et al., 2015).

The term “reactive surface area” or “RSA” as defined here is primarily a concept (and thus a parameter) that is used in continuum reactive transport models (Steeffel et al., 2015a). In the continuum treatment of water–rock and water–soil processes, a representative elementary volume (REV) is defined that consists of an assortment of mineral grains packed together with some pore structure. Individual reactive sites and even individual mineral surfaces in the continuum approach are not normally resolved (Molins, 2015). Instead, average values (Maher et al., 2009) or a distribution of values (Liu et al., 2015) are used (Fig. 1). This approximation is necessary because the detailed reactive site distribution is not available in natural systems as it may be on a single mineral grain in an Atomic Force Microscopy (AFM) study (Teng et al., 2000; Bracco et al., 2013). The total reactive surface area used in continuum scale reactive transport models serves as a proxy for

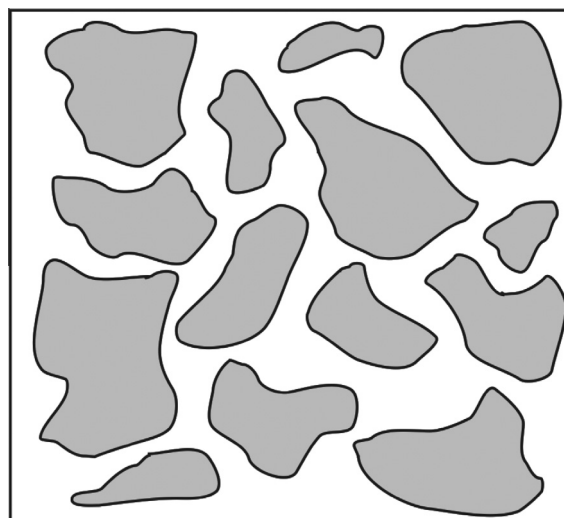


Fig. 1. Schematic representation of a representative elementary volume (REV) in a continuum reactive transport model. In the continuum approximation for mineral reaction, an average value for the reactive surface area is used.

the actual concentration of reactive sites on the mineral. However, in conventional experimental rate determinations (e.g., a well-mixed flow-through reactor), the rate is normalized to the physical surface area (e.g., through the use of a BET determination) and the site density is assumed to be implicit in the rate constant.

Currently, the commonly utilized reactive transport models used to describe fate and transport in subsurface materials (Steeffel et al., 2015b) make use of a single value of the reactive surface area that is intended to capture the average reactivity of each mineral phase, A_m (m² mineral/m³ porous medium), according to Steeffer and Lasaga (1994):

$$R_m = A_m k [f \Delta G_r] \quad (1)$$

where k is the rate constant and $f \Delta G_r$ is some function of Gibbs free energy, or the thermodynamic driving force for the reaction. The bulk reactive surface area, A_m , is related to the more typically measured specific surface area by,

$$A_m = (SSA \cdot \phi_m \cdot M_w \cdot V_m^{-1}) \quad (2)$$

where SSA is the specific surface area of the mineral (m²/g), ϕ_m is the mineral volume fraction (m³ mineral/m³ porous medium), M_w is its molecular weight (g/mol), and V_m is the molar volume (m³/mol).

Currently, there is no universally accepted method for estimating average mineral reactive surface areas. Consequently, a range of approximations have been developed based on easily measurable attributes. The goal of this work is to evaluate these reactive surface area approximations on mineral dissolution rates by comparison between modeling and experimental results. The simplest approach estimates reactive surface area as geometric surface area (GSA), assuming a single grain diameter and spherical or cubic geometry for all minerals (Steeffel and Lasaga, 1994; Steeffer and Lichtner, 1998; Gunter et al., 2000) or two distinct grain diameters, one for clay minerals and one for

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