

Reactive-transport modeling in water film in rock pores: Implication to the dissolution of water-unsaturated rock

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Mineral-water reactive surface area is essential for considering water-rock interaction. Because water and air often coexist in rock pores in the vadose zone, the reactive surface area in the rock under water-unsaturated conditions may be smaller than that under saturated condition. However, our experiments using Fontainebleau sandstone (porosity: 6%, mineral composition: quartz ~100%) and porous rhyolite (porosity: 18%, glass 87%, plagioclase 9%, quartz 4%) demonstrated that almost the same amounts of dissolved element (= [dissolution rate constant (mol/m²/s)] x [reactive surface area (m²)] x [reaction time (s)]) were obtained under saturated and unsaturated conditions, which shows that the reactive surface area was unaffected by the decrease of water saturation. This result indicates that almost all the surfaces of air-containing pores were wetted with water film and thereby dissolution occurred. The results also suggest that the rate of flushing of dissolved element to the outside of the water film was fast enough to keep the concentration in the film far lower than the equilibrium concentration of the mineral, because the mineral dissolution rate usually decreases if the concentration approaches equilibrium. To quantitatively understand the reaction and the transport in water film and to elucidate the factors that may affect these phenomena, we constructed a reactive-transport model considering the dissolution and diffusion occurring in the water film.

First, we estimated the water film thickness h (m) that is an important parameter for modeling reactive transport in the film. Theories for estimating the relationship between film thickness and relative humidity have been developed on the basis of van der Waals force and electric double layer force acting between air-water film-mineral. We applied the theories and derived the expression for predicting the thickness of water film in equilibrium with the relative humidity in air-containing pores. By using the expression, the film thickness was revealed to depend mainly on pore diameter d_{pore} (m). For Fontainebleau sandstone having pore diameters of 6-42 micrometers, the film thicknesses were estimated to be 7-20 nm. Next, by considering the mass balance in the water film, the following formula is obtained:

$$dc/dt = D(d^2c/dx^2) + k(A/V_{film})(1 - c/c_{eq})$$

where c (mol/m³) is the solute concentration in the film, t (s) is the time, x (m) is the position, D (m²/s) is the diffusion coefficient, k (mol/m²/s) is the dissolution rate constant, A (m²) is the reactive surface area, V_{film} (m³) is the volume of the film, and c_{eq} (mol/m³) is the equilibrium concentration. By analytically solving the above formula, we obtained the expression of the concentration profile formed in the water film at the steady-state. It was found that the concentration depends on film thickness, diffusion length (~grain size), surface roughness, diffusion coefficient, and type of mineral (k and c_{eq}). The thicker the water film, the faster the flushing rate and the lower the concentration in the film. The concentrations of Si in water film calculated for Fontainebleau sandstone were found to be significantly lower than c_{eq} of quartz ($<0.03 c_{eq}$), which is consistent with the experimental result.

Finally, by applying the model presented in this study to sedimentary rocks with various pore structure and mineral composition, we evaluated the condition of the film thickness (pore diameter) and the grain size required for keeping the concentration in the water film to be far lower than equilibrium concentration. If a rock of interest has pore diameters and grain sizes that satisfy the required condition, the surface areas available for dissolution are the same between water-saturated and unsaturated conditions. Such criteria would be useful to evaluate the reactive surface area under unsaturated conditions.

Keywords: reactive surface area, reactive-transport modeling, water film, unsaturated condition, dissolution