Effect of Intensity and pH of Rain on the Dissolution of Limestone

A.K.M. Adham, Akira Kobayashi
Graduate School of Agriculture, Kyoto University
Kyoto, Japan

ABSTRACT

The effect of intensity and pH of rain on the dissolution of limestone was observed by using numerical simulation. Results showed that the rate of dissolution of limestone in natural environments may be influenced by both transport and surface-reaction process. When the acidification of the rain water progresses, the dissolution of limestone increases specially at shallow areas. Increase of intensity of water, which coincides with the increase of velocity of inlet water, caused the less increasing dissolution rate of limestone, while the transports of chemicals were increased.

KEY WORDS: Limestone; dissolution; pH; intensity; rainwater; chemical reaction; transport

INTRODUCTION

Chemical dissolution of bed rock/minerals (limestone) plays a central role in determining the geochemistry of natural waters. The major source of dissolved species to natural water is the rocks coming in contact with water. As soon as the rocks come into contact with water, water–rock reaction starts and moves forward towards equilibrium by dissolving or leaching bedrock minerals into the solution. The solute concentration in the water system is proportional to the reactivity of the bedrock minerals constituting the catchment (Yadav and Chakrapani, 2006). Natural waters from carbonate aquifers have been identified as undersaturation with respect to calcite. This undersaturation suggests that the dissolution kinetics of calcite in natural environments may be relatively slow and may play an important role in the chemical evolution of groundwater systems in carbonate rocks (Langmuir, 1971).

The dissolution rates of limestone in CO$_2$ containing aqueous solutions are determined by three rate-containing processes: (1) the kinetics of dissolution at the mineral surface, which depends on the chemical composition of the solution at the liquid-rock boundary; (2) mass transport by diffusion away from this boundary for the dissolved material Ca$^{2+}$, HCO$_3$-, and CO$_3^{2-}$, and towards this boundary for the reactant CO$_2$; and (3) conversion of CO$_2$ into H$^+$ and HCO$_3^-$ (Kaufmann and Dreybrodt, 2007). The rate of dissolution of any mineral is dependent upon the rate of transport of reactants and products between the mineral surface and the bulk solution, the rate of heterogeneous reaction at the mineral surface, and, possibly, on the rates of homogeneous reactions within the solvent. Depending upon the hydrodynamic and chemical characteristics of the environment, one or all of these processes may be important in determining dissolution rate (Plummer and Wigley, 1975). In order to predict the rates of chemical evolution of natural water systems in contact with limestones, it is important to determine the conditions under which calcite dissolution is transport-controlled and those under which dissolution is reaction-controlled.

The transport of dissolved chemical species through a water saturated porous medium is influenced by a wide variety of reversible and irreversible chemical and physical processes, including dispersion/diffusion, advection, formation of complexes in the aqueous phase, sorption, and chemical precipitation. Existing models which incorporate certain individual chemical processes suffer from omission of other possibly significant processes. Thus, the reliability of predictions made through the application of these models is, at best, difficult to assess (Miller and Benson, 1983).

Several studies of limestone dissolution have been carried out. Sjoberg and Richard (1984) observed temperature dependent of calcite dissolution kinetics between 1 and 62 °C at pH 2.4 to 8.4 in aqueous solutions. Liang et al. (1996) experimentally investigated the dissolution kinetics at the calcite-water interface. Nierode and Williams (1971), and Berner and Morse (1974) have shown experimentally that transport processes play an important role in the rate of dissolution of calcite in stirred solutions of dilute acids in which the pH is less than 4. Above pH 4, dissolution in stirred solutions is considerably slower than that predicted by simple transport process models and is thought to be primarily determined by the kinetics of surface reaction(s).

On the other hand, the pH and intensity of rain is changing due to global warming. So for changing such parameters, it is also changing the chemical reaction with other elements. As acid rain causes the dissolution of carbonaceous stones so determining those effects is very important for the stability of the underground dam construction in the limestone, which is the main geology of the Islands having the underground dam in Japan, as well as increasing pollution into the ground surface specially groundwater contamination. So the objective