Carbonate dissolution along fractures of sandstone aquifers: field observations and modelling

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Abstract Fractures in carbonate-cemented Triassic sandstone (Middle Keuper, southwest Germany) show characteristic dissolution seams resulting from the buffering of natural acid solutions. Width and depth range of this carbonate leaching depend among other factors on the aperture of the fractures, the water/rock reaction kinetics and the time period of substantial groundwater circulation. Experiments in the laboratory have demonstrated that diffusive transport from the reaction front within the fracture adjacent matrix plays in important role in the formation of the dissolution seams, but advection of groundwater within the leached, porous dissolution seams of the matrix appears to be the main factor in controlling carbonate dissolution. Using known rates of carbonate denudation for humid climate, the penetration of Holocene (10 000 years) carbonate leaching from the fracture walls into the matrix of a sandstone aquifer is calculated for a simplified field model. A better understanding and quantification of these processes not only allows the reconstruction of the evolution of specific sandstone aquifers, but is also a prerequisite for the prediction of groundwater acidification risks, e.g. by acid rain or acid mine tailings.

INTRODUCTION

Long-term dissolution (and precipitation) processes along the fractures of both carbonate-bearing and carbonate-free rocks control to a large degree the evolution of lithified aquifer systems and their groundwater chemistry. In addition, manmade acid rain and its impact on forest vegetation, soils, and groundwater quality have become serious problems. The question is where and to which extent rock aquifers are affected by natural and anthropogenically increased proton input. Carbonate-bearing rocks have a high acid neutralization capacity which appears to be little limited by rock/water reaction kinetics, but the effects of carbonate dissolution on the properties of the aquifer system can be substantial after long time periods of groundwater circulation. Groundwaters from silicate rocks are frequently not completely buffered and thus testify that the percolating water has not sufficiently reacted with the rock minerals (cation exchange and silicate weathering). In the crystalline rocks and the Triassic Bunter sandstone of the Black Forest, southwestern Germany, for example, acidic soil water is generally buffered to a large degree on its way through the underlying fractured rocks (Fig. 1, Hinderer, 1994), whereas shallow groundwater of periglacial debris layers (frequently perched groundwater) is normally found to be acid at its discharge. In this study we examine the role of carbonate cement of sandstones in the long-term buffering of proton input.
GENERAL CONCEPT AND PREVIOUS WORK

The dissolution processes of the carbonate cement in a fractured porous sandstone can be summarized as follows: within the matrix, adjacent to a fracture, a solution front (boundary between fresh, tight matrix and carbonate-depleted zone) develops, progressing further into the matrix with time (Fig. 2). The rate of advance of this front

Fig. 1 Proton net input and proton buffering rate in soil, regolith, fractured Bunter Sandstone and granite in the Seebach catchment area (northern Black Forest, southwest Germany) (Hinderer, 1994).

Fig. 2 Conceptual model of groundwater flow in a fractured, more or less porous sandstone, illustrating the dissolution process of the carbonate cement in the matrix.
depends on the matrix properties of the carbonate-depleted zone (solution seam), such as porosity, permeability, tortuosity, the fracture geometry (i.e. aperture, roughness), the hydraulic potential distribution, and the reaction chemistry of the carbonate system (kinetics). The rate of advance increases with the fracture flow rate, providing the upkeep of the maximum concentration gradient between the solution front and the fracture water. In a narrower fracture it can be visualized that the solution front does not penetrate the matrix any further, once the water in the fracture has reached saturation with respect to calcite; then dissolution ceases.

A number of field observations (e.g. Douveas, 1990) show that these processes occur at different intensities. Larger fractures with high groundwater flow rates display wider dissolution seams as compared to narrower fractures, where the dissolution of the matrix cement advances at considerably slower rates. To the authors’ knowledge, no systematic investigations into this phenomenon exist.

The chemical processes, occurring in the fractures and the pore space of a porous fractured rock, affect not only the water quality but also the hydraulic properties of the rock. Such processes have been studied, for example, within the context of the genesis of uranium deposits and their subsequent leaching properties during mineral exploitation (e.g. Bennett et al., 1992; Come & Chapman, 1991). For the risk assessment of nuclear repositories, the complex chemical processes, coupled with groundwater flow and solute transport have been studied extensively (e.g. Tsang, 1987). Frequently, these assessments rely heavily on the retarding and immobilizing influence of the matrix (matrix diffusion, chemical interaction between contaminant and matrix material). Further studies relevant for the processes here are investigations into hydrothermal interaction between reactive fluids and the surrounding rock (Norton & Kapp, 1977). Although the diagenetic cementation of sandstones had been extensively studied by geologists and geochemists, the reverse process, i.e. the deeply reaching weathering of sedimentary rocks, has been examined less frequently.

There are a number of theoretical and modelling studies, evaluating the effect of the chemical leaching of fractured porous systems (e.g. Read et al., 1993; Novak, 1993). However, experimental studies are rare and mainly concentrate on processes occurring within a single fracture (Cliffe et al., 1993; Marone et al., 1988; Andersson, 1990; Hung et al. 1989; Morrow et al., 1990) or only within the porous matrix (e.g. Fabriol et al., 1993). In order to examine the effects of acid rainwater on the stability of concrete structures, James (1992) looked at a similar system as the one described in Fig. 2. They investigated the influence of the dissolution of the cement matrix on the weakening of the concrete structure.

In this paper, field observations and first results of experimental and modelling studies, describing the dissolution of carbonate cement in a fractured porous system, are presented and compared with a simplified field model.

FIELD OBSERVATIONS

The matrix dissolution processes in a fractured porous system were studied in the field in an abandoned quarry (Gschwend, southwest Germany) were carbonate-rich sandstones of the Middle Keuper were mined. It mainly consists of thick arcosic sandstone beds, intercalated with thin shale layers. The fresh, unweathered sandstones show carbonate contents of ca. 40% (weight). The porosities vary between 2% and 3.4%, hydraulic con-
ductivities between $1.8 \times 10^{-11}$ and $3 \times 10^{-12}$ m s$^{-1}$. The apertures of the fractures and the thicknesses of the solution seams were measured (Fig. 3) in order to provide evidence for the above model. Contrary to what was expected, the thicknesses of the solution seams decrease with an increase in fracture aperture. This is due to the fact that, as soon as the carbonate cement is dissolved, the rock disintegrates and single sand grains are flushed out of the system. An average residual carbonate content of ca. 20% was determined in thin sections and by chemical analysis of material from solution seams.

**DIFFUSION EXPERIMENTS**

It is believed that, apart from advection within the fractures and in the higher permeable matrix, diffusion processes contribute considerably to solute transport, especially when the leaching of the carbonate cement is further advanced into the rock matrix. In order to investigate diffusion controlled processes with a moving boundary and a change in the diffusion coefficient with time, experiments were conducted in a diffusion cell (Fig. 4). One of the reservoirs contained hydrochloric acid of different pH ($pH = 1$ and $pH = 2$), the other contained an isomolaric solution of potassium iodide to prevent osmotic effects. The diameters of the samples were 4.6 cm and their thicknesses varied between 0.5 cm and 1 cm. The change of mass of calcium and iodide with time were measured in the acid containing reservoir, and the effective diffusion coefficients for $H^+$ could be determined by applying the shrinking core model (Hinsenburg, 1993) according to the following equation (1). In the model the flux of hydrogen ions towards the reaction front, which follows Fick’s first law, is balanced by the flux of hydrogen ions required to dissolve the calcite along the distance interval $dl$ per time interval $dt$ (Figs 4 and 5).

$$m_{\text{Ca}} = \frac{2D_{e(H^+)}C_{H^+}C_0^2t}{\beta}$$

The concentration of calcium in the rock ($C_0$), the acid neutralization capacity of the rock (beta), i.e. the amount of acid required to dissolve the calcite, and the concentration of $H^+$ ($C_{H^+}$) can be measured independently. Plotting the cumulative mass of Ca$^{2+}$
against the square root of time leads to a straight line and from the slope of the straight line to an estimate of the effective diffusion coefficient ($D_e$) of $H^+$. With this information, and information on the effective porosity and the free water diffusion coefficient of $H^+$, the tortuosity factor ($l/l_c^2$) and the advance of the solution front can be determined. The average $D_e$ of the seven rock samples was $4.3 \times 10^6$ cm$^2$ s$^{-1}$ which varies between $2.9 \times 10^6$ and $5.5 \times 10^6$ cm$^2$ s$^{-1}$. The average tortuosity factor was calculated at 6.5 and varies between 4.9 and 9.4. Both parameters appear to be independent of pH and thickness of the sample. The results compare well with the parameters, determined by Mauch (1993).

The data were used to model the advance of the solution front into the rock matrix with time (Fig. 6). The assumed equilibrium concentration of calcite ($C_{CaCO_3(eq)} = 0.27$
g l⁻¹) is equivalent to a calcium concentration of $C_{\text{Ca}^2+_{(\text{eq})}} = 2.68 \text{ mmol l}^{-1}$. This corresponds to an initial partial pressure of $p_{\text{CO}_2} = 10.4 \text{ kPa}$ for $10^\circ\text{C}$. Before the water reaches the entry of the fracture, calcite has already been leached in the debris layer and at the top of the sandstone. For this reason, the input concentration for the diffusion limited fracture model is assumed (1) $C_{\text{Ca}^2+_{(0)}} = 1.07 \text{ mmol l}^{-1}$ or (2) $C_{\text{Ca}^2+_{(0)}} = 1.60 \text{ mmol l}^{-1}$. The remaining carbonate denudation rate is for (1) 60% and for (2) 40% of the initial carbonate denudation rate. The value of 40% (areal denudation rate of 20 cm per 1000 years) is also taken in the following field model (Fig. 7). The diffusive flux of $\text{Ca}^{2+}$ from the rock matrix into the fracture and the resulting advance of the solution front was calculated at discrete space and time intervals, based on estimates of the fracture aperture, $\text{CO}_2$ partial pressure in the soil, and the parameters determined experimentally.

**SIMPLIFIED FIELD MODEL**

In order to get an initial estimate of the maximum advance of the solution front, the following simplified model of a carbonate-cemented sandstone was examined (Fig. 7). The sandstone is covered by a debris layer with a carbonate content of 20% (volumetric) and has a total porosity of 50%. The underlying sandstone has a carbonate concentration of 40% (volumetric) in its matrix and is evenly fractured (orthogonal fractures). The entire system is subjected to carbonate dissolution for a time period of 10 000 years (corresponding to the Holocene). For reasons of simplicity it is assumed that first the carbonate content of the debris layer and along the top of the sandstone is evenly leached, before dissolution penetrates into the fracture system of the sandstone, but carbonate-leaching can also occur simultaneously in these different zones. For the dissolution of carbonate cement along the rock fractures two alternatives are discussed, (I) with a level of discharge at 20 m and (II) at 100 m below ground level. Assuming an equilibrium concentration of 270 mg l⁻¹ CaCO₃ for humid climate with dense, permanent
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Fig. 7 Simplified leaching model of a carbonate-cemented fractured sandstone (maximum rate of advance, no diffusion or advection limitation). Calculations based on a denudation rate of 0.5 m per 10 000 years for pure calcite. Groundwater circulation is assumed to affect either 20 m depth (level I) or 100 m depth (Level II); circulation period 10 000 years. R, residual carbonate cement after 1 million years.

vegetation cover, groundwater recharge of 500 mm year\(^{-1}\), and immediate removal of carbonate solution (i.e. no diffusion limitation), an average denudation rate of 5 cm per 1000 a or 50 cm per 10 000 years can be calculated. After 20 cm of the total "denudation capacity" of 50 cm per 10 000 years is used up to dissolve the carbonate in the debris layer and 10 cm per 10 000 years for the calcite along the top of the sandstone, the remaining 20 cm per 10 000 years are used for dissolution of the carbonate cement in the fracture walls. With the discharge level I at 20 m below ground level (i.e. no further dissolution beyond this depth), the average penetration of the solution front into the fracture walls is 1.25 cm. With the discharge level II at 100 m below ground level, the average penetration is 0.25 cm after 10 000 years. For a time period of 1 million years, approximately one half of the carbonate cement of the sandstone (discharge level II) is leached.

**DISCUSSION**

The values gained from the pure diffusion model and those from the simplified field model can be compared, because the controlling factors were the same (carbonate content, porosity, length of the fracture affected, "denudation capacity" of the percolating water after passing the debris layer, etc.). In the simplified field model the solution front progrades, on the average, faster (2.5 mm per 10 000 years for level II,
Fig. 7) from the fractures into the rock matrix than according to the data gained from
the diffusion-limited experiment (ca. 2 mm per 10 000 years, Fig. 6). The reason for
this difference, which increases when regarding longer time periods, is that the leaching
process is also determined by advective transport within the solution seam, thereby
accelerating the removal of carbonate from the matrix. Average hydraulic
conductivities, measured on field samples of the solution seam, were as high as 1 \times 10^{-6}
m\ s^{-1}. In sandstones with less carbonate cement than in our examples, the solution front
will prograde faster from the fractures into the matrix. Presently, a model, which also
includes advective transport in the matrix, is being built. This model will be validated
by reactive flow experiments through sandstone fractures of varying aperture.

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