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Changes in reactive surface area during limestone dissolution: An experimental and modelling study

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ABSTRACT

This study explores the dynamics of porosity and reactive surface area changes during porous limestone dissolution by CO_2-rich water. The Sr and Ca concentrations in both the rock and the outlet solution are used to evaluate the reactive surface area changes of the two rock-forming calcites, i.e. micrite grains and sparite crystals, which have different trace element signatures. The geometric surface area measured with X-ray microtomography decreases slightly whereas the reactive surface area increases continuously with increasing porosity from 20.3 to 30.2%. Surprisingly, changes in reactive surface areas are very different between the two calcites. The reactive surface area changes in the micrite are parabolic while the reactive surface area of sparite increases greatly. The numerical model HYTEC is used to model the change in reactive surface areas during the experiment. Different geometrical models are tested. The model based on spherical-grain dissolution and spherical-pore growth fails to reproduce the experimental results, while the sugar-lump model provides reasonable agreement with the experiment.

1. Introduction

Chemical reactions are common in geological reservoirs and thus may induce mineral dissolution (or precipitation). Porosity increase associated with mineral dissolution is an important process in a range of geological settings and industrial applications including diagenesis, karst formation, well stimulation and carbon dioxide sequestration (e.g. Holloway, 1997; Kaufmann and Braun, 1999; Bachu and Adams, 2003). Long-term sequestration of carbon dioxide (CO_2) in geological formations is a current challenge, given the complexity and range of coupled thermal, hydrological, mechanical, and chemical processes involved. Among others, massive injections of CO_2 into reservoirs may alter the geochemical equilibrium between rock-forming minerals and formation waters. Changes in the solid phase volume lead to rock structure modifications, affecting both flow and transport properties of the porous media. Understanding the interplay between chemical reactions, rock geometry changes and fluid transport properties is critical to achieve better predictions of the CO_2 fate in reservoir rocks.

Chemical interactions between minerals and water are driven by chemical disequilibria that persist in the system. Dissolution occurs when fluids are undersaturated with respect to some minerals, i.e. the ionic activity product is lower than the equilibrium constant. During CO_2 injection into host reservoirs, changes in chemical conditions can occur locally due to CO_2 dissolution in the brine present in the reservoir. Coupled with other changes (e.g. temperature and fluid pressure), an increase in CO_2 partial pressure (P_{CO2}) favours particularly the dissolution of carbonate minerals (e.g. Stumm and Morgan, 2004). Thus, massive injection of CO_2 into a carbonate host reservoir can induce strong dissolution of the matrix and porosity increase.

Porosity changes can be calculated from the volumetric amount of dissolved minerals, which is closely related to mass balance. However, the description of macroscopic dissolution patterns is very complex, since they are influenced by several factors including rock heterogeneities, chemical reaction kinetics and mass transfer (e.g. Steefel and Lasaga, 1990; Jamtveit and Yardley, 1997; Lichtner et al., 1997). In some cases the porosity increase is uniform whereas in other cases, it is localised. As a consequence, flow and transport properties can be dramatically different. A number of experimental and theoretical studies have analysed the influence of dissolution processes on the physical and chemical properties of porous media (e.g. Schechter and Gidley, 1969; Fogler and Rege, 1987; Hoefner and Fogler, 1998; Noiriel et al., 2004). For instance, leading mechanisms, such as pore coalescence (Schechter and Gidley, 1969) and formation of highly

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conductive flow channels (Daccord et al., 1993; Renard et al., 1998; Golfier et al., 2002) involve particularly complex feedback effects.

Among the parameters that measure how important is the interaction between chemistry and flow, the Damköhler number ($Da = k_d L^* / u$, where k_d is a first-order rate constant [s^{-1}], L^* is a characteristics length [m] and u is the fluid velocity [m s^{-1}]), accounts for the relative contribution of advective transport and chemical reaction in the mass transfer process. At high *Da* (far from equilibrium), dissolution tends to be dominated by wormhole formation. In contrast, at low *Da* (for example, when the fluid comes to equilibrium), the dissolution becomes more uniform (Golfier et al., 2002).

While great progress has been made in the understanding of the coupling of chemical reaction kinetics and chemical mass transfer, many fundamental problems remain to be solved before long-term predictions can be envisaged. In particular, reactive transport models may fail to reproduce laboratory experiments or field observations when chemical and flow gradients are strong or porous medium is heterogeneous (Glassley et al., 2002; Meile and Tuncay, 2006). Most reactive transport models follow a macroscopic approach, using equivalent properties averaged at the scale of a representative elementary volume (REV). This allows to solve the mass and energy balance of the chemical system for a homogeneous mixture of liquid, solid phases, aqueous species and, possibly, gases. The pore structure geometry and the spatial arrangement of the different rock-forming minerals are often represented in an abstract manner and the numerical models conceived at the macroscopic scale fail to describe the spatial arrangement of the minerals and pores. Thus, the influence of geometry is most likely underestimated in reactive transport modelling. Improvements in non-invasive 3D imagery allow predictions of macroscopic flow properties from microscopic image data (Bernard, 2005; Fredrich et al., 2006), but modelling of pore-scale reactive transport processes and upscaling them to a macroscopic scale are not yet common practice, despite some recent new developments (Li et al., 2007; Li et al., 2008; Flukiger and Bernard, 2009-this issue). Pore-scale models are essential to bridge the gap between pore-scale observations and feedback mechanisms occurring in the macroscopic environment. However, microscopic information is available, and some pore-scale processes can be taken into account in an integrated manner at the REV scale, i.e. the relationship between porosity, permeability and the liquid-exposed surface area of the matrix-forming minerals.

The aim of this study is to understand the dissolution of a porous limestone which involves a significant change in the reactive surface area as well as in the hydrodynamic properties of the medium including porosity and permeability. All these properties are closely linked to the coupled chemistry-transport processes and the modelling therefore requires a fully coupled approach. Experimental work was carried out to provide datasets, according to a methodology combining chemical analyses of the fluid, chemical characterisation of the solid rock, continuous measurements of the permeability and periodic characterisation of the sample geometry by non-invasive X-ray microtomography. Measurements of major and minor elements both in the solid rock and the outlet solution are used to quantify reactive surface area changes for the two rock-forming calcites, i.e. sparite crystals and micrite grains. The reactive transport code HYTEC was used to model the experiment, and different models for reactive surface area evolution were examined.

1.1. Surface areas of rocks

The reactive surface area is an important parameter, because the mineral–fluid interface partially controls the kinetic behaviour in many geological systems. Thus, the characterization of reactive surface area changes resulting from dissolution or precipitation is a prerequisite to accurate modelling of reactive transport in porous media. Let us consider the dissolution of calcite, for which it is generally admitted that the equation describing the dissolution rate is (Lasaga and Kirkpatrick, 1981):

$$r = S_r \times k_c \times (1 - \Omega_{cal}) \tag{1}$$

with r the calcite dissolution rate (mol s^{-1}), S_r the reactive surface area of the mineral (m^2), k_c the overall kinetic dissolution rate (mol m^{-2} s^{-1}) and Ω_{cal} the calcite saturation index. It is worth noting that, in numerical simulations, the surface area often refers to a specific surface area, i.e. one that is normalized to a volume of water (m^2 m^{-3}). Far from equilibrium and in the absence of inhibiting species, k_c can be described following Plummer et al. (1978):

$$k_c = k_1 a_{H^+} + k_2 a_{CO_2} + k_3 \tag{2}$$

with a_i the activity of the species i, k_1, k_2 and k_3 the kinetic rate constants equal to 5.12×10^{-1}, 3.45×10^{-4} and 1.19×10^{-6} mol m^{-2} s^{-1}, respectively at 25 °C. Far from equilibrium and at low pH, the dissolution rate depends essentially on the pH and the reactive surface area.

In the absence of mass transfer changes (i.e., the mass transfer is in steady-state), a change of the dissolution rate is possible due to the variation of the reactive surface area, as chemical reactions proceed. The problem is that the reactive surface area on minerals is generally not directly measurable. Moreover, as dissolution occurs at selected sites on the minerals, the reactive surface area may be smaller than the geometrical surface area (Helgeson et al., 1984). That is why this parameter is often used as a fitting parameter in reactive transport codes (Brosse et al., 2004). Nevertheless, the reactive surface area can be estimated from phenomenological or empirical laws, even if the choice of an adequate surface model is still a matter of debate (Gautier et al., 2001; Lüttge et al., 2003). Most of the models are based on total surface area measurements linked to gas adsorption (Brunauer et al., 1938) or to geometrical constructions (Canals and Meunier, 1995; Le Gallo et al., 1998; Colon et al., 2004). Measurements of the surface area by vertical scanning interferometry, atomic force microscopy, laser confocal microscopy or X-ray tomography are sometimes proposed (e.g. Fredrich et al., 1993; Shiraki et al., 2000; Lüttge et al., 2003; Noiriel et al., 2004). However, the applicability of the experimental values in reactive transport models is limited, since the geometrical surface area strongly depends on the scale at which the process is observed. Nevertheless, expressions based on geometrical constructions remain the most practical to compute surface area changes in geological systems by modelling.

A number of different models based on geometrical constructions have been proposed to relate changes in mineral concentration (or porosity) to changes in reactive surface area (Lichtner, 1988; Emmanuel and Berkowitz, 2005). The simplest representation of a porous medium is a package of spherical grains. If it can be assumed that the porous medium is composed of floating spherical grains, the reactive surface area can be expressed by:

$$S_r = S_{r0} \left(\frac{C}{C_0} \right)^{2/3} \tag{3}$$

where C is the mineral concentration, C_0 the initial mineral concentration and S_{r0} the initial surface area. This model assumes a homogeneous decrease of the grain size with dissolution. Alternatively, it can be assumed that the porous medium is represented by floating spherical pores. Thus, an increase of the reactive surface area with dissolution is expected, according to the following law:

$$S_r = S_{r0} \left(\frac{C}{C_0} \right)^{-2/3} \tag{4}$$

A porous medium can also be represented as a cluster of particles, which dissociate as dissolution progresses, exactly as a sugar lump in a