



# Changes in porosity, permeability, water retention curve and reactive surface area during carbonate rock dissolution



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## ABSTRACT

Chemical reactions between fluids and the solid phase change porous media by dissolution and precipitation processes that modify the pore space geometry and associated hydraulic and chemical properties (saturated and relative permeability, porosity, capillary pressure curve, pore size distribution, reactive surface area). Knowledge of these properties and how they evolve with time is important for understanding and modelling multi-phase flow or reactive transport. Most published studies for reservoir rocks concentrate on the changes of porosity and saturated liquid permeability, but few data are available on the other parameters, and even less on their evolution during interaction with acidic solutions.

We investigate the joint evolution of transport parameters of sedimentary carbonate rocks upon reaction with dilute acid (HCl). We first characterize the initial permeability, porosity and pore size distribution. We then attack the rock samples by permeation with HCl (pH 3.5 or 4.1) and characterize them again after partial dissolution. Several dissolution-characterization cycles were performed on each sample in order to study the evolution and interaction of the different parameters.

In two coarse calcite cores C1 (dissolved at pH 3.5) and C2 (pH 4.1) with high initial permeability, significant dissolution occurred only in pores with diameters greater than 0.022 mm. Permeability increased very little even though porosities increased by 2.6–5.8%. In fine-grained dolomite cores, dissolution affected a broader range of pore sizes, down to 0.001 mm in D1 (pH 3.5), and down to 0.0066 mm in D2 (pH 4.1). A wormhole broke through in D1 after percolation of only 5000 pore volumes of acid. Effective reactive surface areas decreased by a factor of 240–250 in the cores dissolved at pH 3.5, but only by a factor of 2–25 in the cores dissolved at pH 4.1. A simple 1-D model was unable to simulate the evolution of the reactive surface during wormhole formation. Effective reactive surface area correlated negatively with permeability, and was consistent with the geometric area of the pores that carried most flux, which was calculated from the retention curves.

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## 1. Introduction

Mineral dissolution or precipitation processes caused by the flow of a reactive fluid through a porous medium often produce volume and surface variations at the pore level that change the flow and transport properties at the macroscale, such as saturated and relative permeability, porosity, reactive surface area, capillary pressure curve and pore size distribution (e.g. Noiriel et al., 2009; Saripalli et al., 2001). Multiple feedbacks complicate the interactions between these parameters and constitutive relationships. For instance, changes in porosity and permeability alter the local fluid velocity, which can affect the types and rates of dissolution and/or precipitation reactions that may occur in different

locations of the porous medium (e.g. Andreani et al., 2009). These processes can also change effective reactive surface areas, which in turn will modify reaction kinetics (e.g. Noiriel et al., 2009; Steefel et al., 2005). These interactions play an important role in many reactive transport, vadose zone and multiphase flow problems, including carbonate reservoir acidizing, geological storage of CO<sub>2</sub>, enhanced oil or gas recovery, and geothermal systems (e.g. de Marsily, 1986; Lasaga and Kirkpatrick, 1981; Parmigiani et al., 2011).

Most published studies concentrate on the changes of porosity and saturated liquid permeability (e.g. Bernabe et al., 2003; Izgec et al., 2008; Luquot and Gouze, 2009; Noiriel et al., 2004). Dissolution can be homogeneous or strongly localized. As a consequence, for a given change in porosity, radically different changes can be observed in other flow and transport properties. Different dissolution regimes can be observed depending on the relationship between advection, diffusion and reaction rate (e.g. Fogler and Rege, 1986; Golfier et al., 2002; Hoefner and Fogler, 1988). The ratio of advection to diffusion is

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described by the Péclet number  $Pe$ , and the ratio of reaction to advection by the Damköhler number  $Da$ . Different definitions have been proposed for these numbers. Here we use the notation of [Golfier et al. \(2002\)](#):

$$Pe = \frac{|v_0|l}{D} \quad (1)$$

$$Da = \frac{\alpha l}{|v_0|} \quad (2)$$

where  $|v_0|$  is the inlet fluid velocity,  $l$  is a pore-scale characteristic length,  $D$  is the diffusion coefficient, and  $\alpha$  is the (first order) mass exchange rate of the reaction. [Golfier et al. \(2002\)](#) arbitrarily chose  $l = \sqrt{k}$ , where  $k$  is the intrinsic permeability.

If the reaction is very slow compared to advection or diffusion (low  $Da$ ), uniform dissolution is observed, i.e. the pore walls dissolve almost homogeneously across the percolated porous medium. If advection is much slower than reaction and diffusion (low  $Pe$ ) then compact dissolution occurs, where dissolution occurs only very close to the core inlet face and the fluid that moves further into the porous medium is already in equilibrium with the solid phase. When reaction and advection exceed a certain threshold (intermediate to high  $Da$  and  $Pe$ ), then preferential flow paths (so-called “wormholes”) form in the porous medium. Their formation, shape and degree of ramification involve complex feedback effects (e.g. [Daccord et al., 1993](#); [Fredd and Fogler, 1998](#); [Golfier et al., 2002](#); [Hoefner and Fogler, 1988](#); [Luquot and Gouze, 2009](#); [Renard et al., 1998](#)).

The relationship between porosity and permeability is usually described by the Kozeny–Carman equation, derived independently by [Kozeny \(1927\)](#) and [Carman \(1937\)](#). It considers the porous medium as an assembly of capillary tubes described by the Navier–Stokes equation (Poiseuille flow). [Kozeny \(1927\)](#) derived the following equation:

$$q = w(l/\mu) c (\phi^3/\sigma^2) \quad (3)$$

where  $q$  is the Darcy velocity,  $w$  the unit weight of fluid,  $l$  the hydraulic gradient,  $\mu$  the viscosity,  $c$  a geometric constant,  $\phi$  the porosity of the porous medium, and  $\sigma$  its specific surface area per unit bulk volume of porous material. In combination with Darcy’s law

$$q = -KI \quad (4)$$

this equation relates saturated permeability ( $K$ ) to porosity ( $\phi$ ) via a power law  $K \propto \phi^n$ . Originally the exponent  $n$  was assumed to be 3, but many later studies (e.g. [Bourbie and Zinszner, 1985](#); [Noiriel et al., 2004](#); [Pape et al., 1999](#)) showed that this exponent can actually vary considerably depending on the type of porous medium and the flow and transport conditions. Exponents  $n$  greater than 100 have been observed in experiments where preferential flow bypasses a large fraction of the total porosity ([Noiriel et al., 2004](#)).

[Noiriel et al. \(2009\)](#) and [Gouze and Luquot \(2011\)](#) studied the dissolution of porous limestones to evaluate changes in the reactive surface area as well as in porosity and permeability. Characterization of reactive surface area changes resulting from dissolution or precipitation is a prerequisite to accurate modelling of reactive transport in porous media. Various models based on geometrical constructions have been proposed to relate changes in mineral concentration and the reactive surface area ([Emmanuel and Berkowitz, 2005](#); [Jove Colon et al., 2004](#); [Lichtner, 1988](#); [Noiriel et al., 2009](#)).

In contrast, hardly any data are available on the changes of pore size distribution and capillary pressure curves due to dissolution reactions, and we did not find a single publication on the joint evolution of all the above flow and transport properties during interaction with acidic solutions, which is essential for adequate understanding and modelling of multiphase flow processes.

In the present laboratory experiments, we investigated the joint evolution of these properties during dissolution of carbonate rocks. After determination of initial hydraulic conductivity, porosity and water retention curve (pore size distribution), four carbonate rock samples were attacked by permeation with HCl (pH 3.5 or 4.1). After partial dissolution, the suite of transport parameters was measured again to study the changes. Several dissolution-characterization cycles were performed on each sample in order to study the evolution and interaction of the different parameters.

## 2. Materials and methods

### 2.1. Samples

Two types of rock were investigated. Samples D1 and D2 are dolomitized oolitic grainstones of white colour from the Campos basin in Majorca, taken from the S22 borehole near Ses Salines, of Upper Miocene age. Based on thin sections and optical microscope observations, they have a maximum grain size of about 0.2 mm and maximum pore diameters of about 0.4 mm (see [Fig. 1a](#)). The mean composition was determined by acid digestion as  $\text{Ca}_{1.14}\text{Mg}_{0.86}(\text{CO}_3)_2$  (molar mass  $M_{do} = 186.6$  g/mol). Samples C1 and C2 are much coarser Lumaquela limestones of beige colour (98.3%  $\text{CaCO}_3$ , with 0.7% Fe and traces of Mg and Si) originating also from Majorca, of Miocene age. They are composed of fragments of the shells of bivalves and other molluscs; poorly cemented, with a maximum fragment size of about 1.5 mm and maximum pore diameters of about 1.2 mm (see [Fig. 1b](#)).

Cores of 25 mm diameter were cut from both materials, and mounted into PVC sleeves (outer diameter 32 mm, inner diameter 27 mm) using Araldit® 7070 high-temperature epoxy resin. Slices of approximately 12 mm thickness were cut from these cylinders and the faces were polished to assure a tight seal between the PVC sleeve and the different experimental setups, described below.

### 2.2. Characterization tests

These experiments consisted of several steps:

- Initial characterization of the samples (triple weight to determine porosity, apparent volume and bulk density; water retention curve; initial permeability)
- Partial dissolution of the samples with dilute HCl and a high flow rate to promote uniform dissolution ([Golfier et al., 2002](#)), and simultaneous measurement of permeability.
- Repetition of the characterization of sample properties.
- Three cycles of dissolution and characterization were carried out on each sample to study the evolution of the parameters and their interactions.

#### 2.2.1. Porosity

Porosity of the rocks was calculated from the weight of the water-saturated sample  $m_{sat}$  and the dry weight  $m_{dry}$  after oven-drying at 40 °C for 48 hours. All weights were measured using a Sartorius® CPA224S precision balance (resolution 0.0001 g).

The pore volume  $V_p$  was calculated as

$$V_p = (m_{sat} - m_{dry}) / \rho_w \quad (5)$$

where  $\rho_w$  is the density of the water used for saturating the sample (1000 kg m<sup>-3</sup>). The gravimetrically determined bulk porosity  $\phi_g$  was computed as

$$\phi_g = V_p / V_s \quad (6)$$

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