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Influence of the flow rate on dissolution and precipitation features during percolation of CO_2-rich sulfate solutions through fractured limestone samples

Maria Garcia-Rios *, Linda Luquot, Josep M. Soler, Jordi Cama

Institute of Environmental Assessment and Water Research (IDAEA), CSIC, Jordi Girona 18, 08034 Barcelona, Catalonia, Spain

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ABSTRACT

Calcite dissolution and gypsum precipitation are expected to occur when injecting CO_2 in a limestone reservoir with sulfate-rich resident brine. If the reservoir is fractured, these reactions will take place mainly in the fractures, which serve as preferential paths for fluid flow. As a consequence, the geometry of the fractures will vary leading to changes in their hydraulic and transport properties. In this study, a set of percolation experiments which consisted of injecting CO_2-rich solutions through fractured limestone cores was performed under $P = 150$ bar and $T = 60$ °C. Flow rates ranging from 0.2 to 60 mL/h and sulfate-rich and sulfate-free solutions were used. Variation in fracture volume induced by calcite dissolution and gypsum precipitation was measured by X-ray computed microtomography (XCMT) and aqueous chemistry. An increase in flow rate led to an increase in volume of dissolved limestone per unit of time, which indicated that the calcite dissolution rate in the fracture was transport controlled. Moreover, the dissolution pattern varied from face dissolution to wormhole formation and uniform dissolution by increasing the flow rate (i.e., Pe from 1 to 346). Fracture permeability always increased and depended on the type of dissolution pattern.

1. Introduction

Carbon dioxide (CO_2) capture and storage (CCS) is considered a potential mitigation option for climate change. It consists of trapping the CO_2 emitted from large point sources and injecting it at depth in suitable storage sites (IPCC, 2005). Deep saline aquifers are one of the preferred types of sites for this purpose (Bachu, 2003; Bickle, 2009; Michael et al., 2010). Currently, in Hontomín (Burgos, Spain), The CIUDEN (Ciudad de la Energía) Foundation has developed a technology demonstration plant for CO_2 storage in a deep saline aquifer where the main reservoir rock is primarily limestone. CO_2 will be injected at a depth of approximately 1500 m. where it will reach supercritical conditions (pressure $P > 74$ bar and temperature $T > 31$ °C) and will react with the resident solution, which is sulfate-rich (at equilibrium with gypsum) and has an ionic strength of 0.6 M. Dissolution of CO_2 into the resident saline solution may induce the dissolution of carbonates (e.g., Gherardi et al., 2007; Nogues et al., 2013; Smith et al., 2013) and because the solution contains sulfate, secondary mineral precipitation (gypsum or anhydrite) may occur. These reactions imply changes in porosity, permeability and pore structure of the repository rocks.

The Hontomín reservoir rock is a fractured system mainly composed of low-permeability rocks (Alcalde et al., 2014), where fractures serve as conduits for flow. In this situation long-lasting flow of fluids in disequilibrium with the rock is expected. Dissolution and precipitation processes can alter the geometry of fractures and, consequently, their hydraulic and transport properties (Noiriel et al., 2013). An aim of this study was to shed light on the fracture dynamics when a CO_2-rich sulfate solution is injected into this type of system.

Predicting changes in the flow and transport properties of fractures is still a challenge due to the complexity of fluid–rock interactions and the uncertain role of fracture heterogeneity. Macroscopic physical properties, such as fracture permeability, are directly related to the microstructure of the fracture, which makes the determination of fracture geometry an important issue to model flow and transport (Gouze et al., 2003; Noiriel et al., 2013; Szymczak and Ladd, 2009). Experiments conducted at the laboratory scale are needed for this kind of characterization. In porous media, the impact of heterogeneities on the evolution of permeability and dissolution patterns has already been evaluated (Carroll et al., 2012; Izgec et al., 2010; Kalia and Balakotaiah, 2009; Luquot et al., 2014; Panga et al., 2005; Smith et al., 2013; Ziauddin and Bize, 2007). Smith et al. (2013) performed core-flood experiments involving CO_2-rich brines and carbonate rocks and reported the formation of stable or unstable dissolution fronts depending on the degree of pore space heterogeneity. Their results were further investigated using 3D reactive transport models by Hao et al. (2013).

Several experimental studies have been performed to investigate fracture evolution during dissolution using non-destructive techniques

* Corresponding author.
E-mail address: mgrios3@gmail.com (M. Garcia-Rios).

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(e.g., nuclear magnetic resonance imaging (NMRI), X-ray computed microtomography (XCMT)), which allow characterization of fracture geometry and flow during dynamic experiments (Detwiler, 2008; Detwiler et al., 2003; Dijk et al., 2002; Ellis et al., 2011; Gouze et al., 2003; Liu et al., 2005; Noiriel et al., 2007, 2013). In this study, XCMT was used to characterize changes in fracture volume due to mineral dissolution and precipitation, bearing in mind that sufficient XCMT resolution is crucial to identify the presence of secondary minerals.

Evolution of fracture structure is directly related to fluid flow and mineral dissolution rates. Feedback between fluid flow, solute transport and mineral dissolution may lead to the formation of preferential flow paths (wormholes) under certain flow and reactivity conditions (Szymczak and Ladd, 2009). Experimental studies about dissolution patterns in a variety of porous systems (Golfier et al., 2002; Hoefner and Fogler, 1988) and in single rock fractures (Detwiler, 2008; Detwiler et al., 2003; Dijk et al., 2002; Durham et al., 2001; Gouze et al., 2003; Polak et al., 2004) have already been carried out, but the physicochemical mechanisms behind pattern formation (e.g., influence of heterogeneities, mineralogical diversity in rocks) are not yet understood in detail. Moreover, theoretical and computational models have been developed to predict this physical and chemical alteration of the fractures depending on the relative rates of transport and reaction (Péclet and Damköhler numbers) but only a few of them have been contrasted against experimental data (e.g., Elkhoury et al., 2013). Due to the presence of sulfate in the system, this study can evaluate whether mineral sulfate precipitation has the capacity to modify reported dissolution patterns.

In this study, we present the results of a set of percolation experiments which consist of injecting a CO_2-rich solution through a fractured limestone core under Hontomin reservoir conditions ($P = 150$ bar and $T = 60$ °C). Experiments were performed under different flow rates (from 0.2 to 60 mL/h) to assess changes in fracture properties with increasing distance from the CO_2 injection well (i.e., decreasing velocity). Also, the role of secondary minerals was investigated by varying the sulfate content of the injected solution (sulfate-free and sulfate-rich). X-ray computed microtomography was used to characterize changes in fracture volume induced by dissolution and precipitation processes. In addition, measurement of the pressure difference between the inlet and the outlet of the sample and of the aqueous chemistry enabled the determination of permeability changes and net reaction rates.

2. Materials and methods

2.1. Sample characterization

The sample used in this study was an oolitic limestone with 5% of porosity. It was provided by CIUDEN and belongs to the Bercedo series (Villanueva de Puerta Formation; ALM-09-008, 2010; Pujalte et al., 1998) in which CO_2 injection will take place. According to X-ray diffraction (XRD) analysis, performed using a Bruker diffractometer model D-5005 with Cu-Kα1 radiation, the mineralogical composition of the oolitic limestone is 100 wt.% calcite.

Six cylindrical cores of 9 mm in diameter (d) and ≈18 mm in length (L) were cored side-by-side in the limestone sample (Fig. 1b). The permeability of the rock cores ($k < 10^{-18}$ m^2) was measured by performing a permeability test using the Icare Lab CSS II apparatus (Luquot et al., 2012). Thereafter, a fracture was artificially created by sawing through each core with a circular saw, during which formation of micro-cracks could happen. Nonetheless, as discussed in Section 3.3, their existence did not influence the overall fracture dissolution. To guarantee flow exclusively through the fracture, all fractures were laterally sealed using a fiber glass thread and Duralco 4525 epoxy resin (stable mechanical and chemical properties up to 690 bar, 260 °C and low pH).

MicroRaman spectra, using a Jobin-Yvon LabRam HR 800 apparatus equipped with an Olympus BXFM microscope and using a wavelength of 532 nm, were collected to identify the secondary sulfate-bearing phases in the reacted fractured cores.

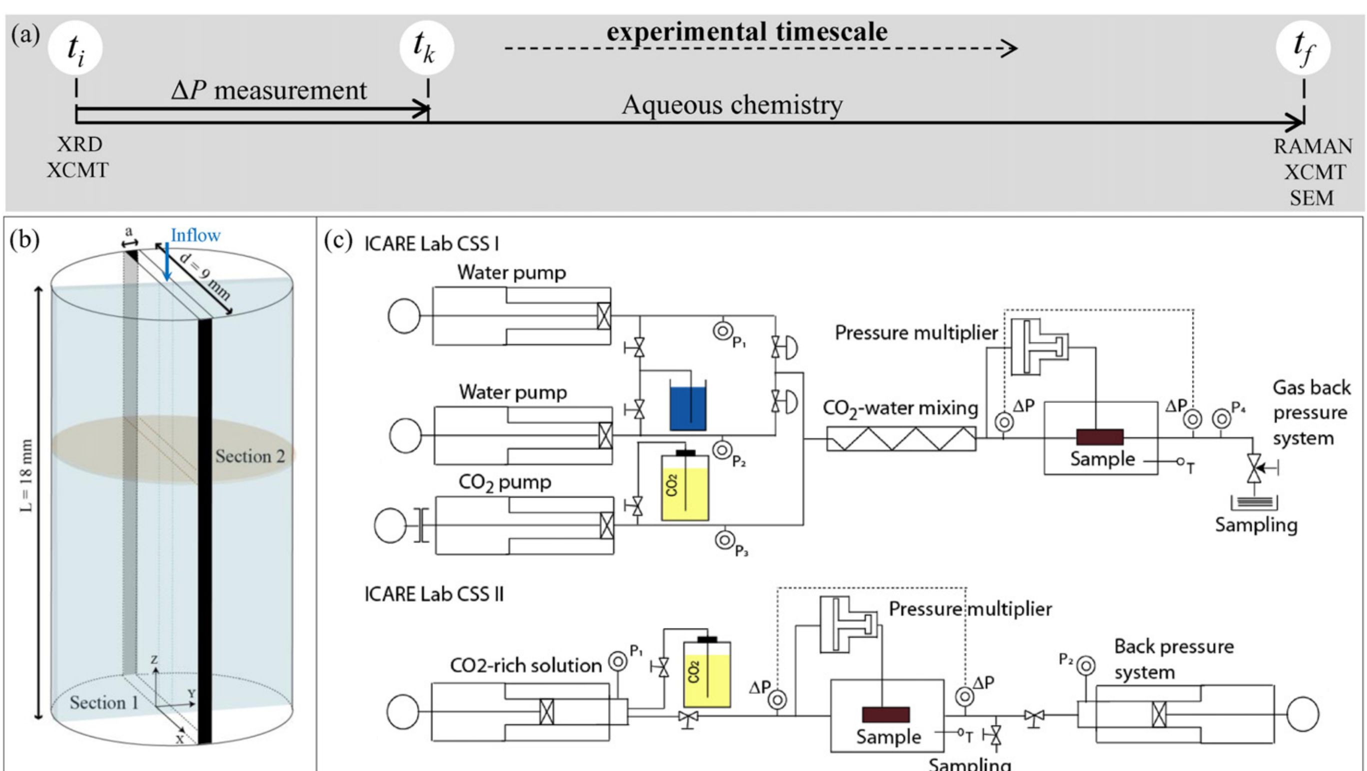

Fig. 1. Scheme of the experimental timescale (a), fractured core dimensions with two section planes perpendicular to the fracture (Section 1 and Section 2 parallel and perpendicular to the flow direction, respectively) (b), and the experimental setups of Icare Lab CSS I and Icare Lab CSS II (c).