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Water Rock Interaction [WRI 14]

Laboratory-scale interaction between CO_2-rich brine and reservoir rocks (limestone and sandstone)

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Abstract

In the laboratory, synthetically fractured cores of limestone and sandstone were reacted with CO_2-rich brines at flow rates ranging from 0.2 to 60 mL h^{-1} and 80 bar pCO_2 and 60 °C (supercritical CO_2 conditions). Interaction between the sulfate-CO_2-rich brines and the primary minerals of the rock caused significant permeability variations. Calcite dissolution was clearly identified and in some case associated with gypsum (or anhydrite) precipitation.

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Keywords: limestone; CO_2 sequestration; dissolution; precipitation; brine; permeability

1. Introduction

The test site for CO_2 injection in Hontomín (northern Spain), is composed of limestones (calcite and dolomite) and sandstones (66 wt% calcite, 21 wt% quartz, 6.5 wt% microcline). CO_2 injection at depth will cause the formation of CO_2-rich acid brines, which will likely promote the dissolution of carbonate minerals (calcite and dolomite). Since the brine contains sulfate, gypsum (or anhydrite at depth) can also precipitate. These sulfate minerals may cover the surface of the dissolving carbonates causing their passivation. These reactions imply changes in porosity pore structure in the repository rocks. Therefore, changes in permeability and fluid flow are expected. Laboratory experiments at 80 bar pCO_2 and 60 °C were carried out to measure the progress of these reactions and the effect exerted on the porosity and permeability of these rocks.

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2. Experimental methodology

A preliminary set of percolation experiments with limestone and sandstone cores (9 mm diameter, 18 mm length, 1 % - 2 % porosity) showed that permeabilities were extremely small (< 1×10^{-18} m^2), not allowing for the injection of the solutions through the cores (Figure 1).

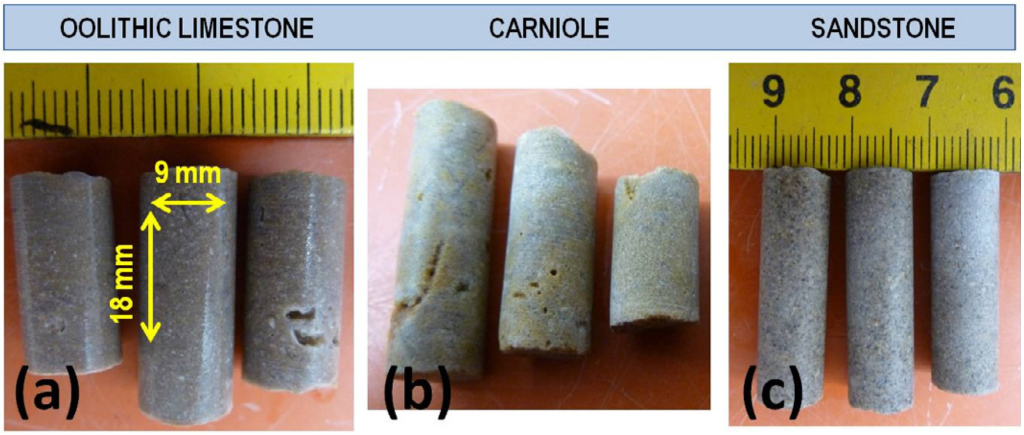

Fig. 1. Type of cores used in the permeability tests: (a) oolithic limestone; (b) carniole (vuggy limestone) and (c) sandstone.

Therefore, it was decided to use fractured rock cores for the experiments. Synthetic fractures were created by sawing the rock cores. Experiments using the fractured cores were performed under CO_2 supercritical conditions (pCO_2 = 8 MPa and T = 60 °C). A synthetic sulfate-rich brine nearly equilibrated with respect to gypsum was injected at different flow rates (0.2 to 60 mL/h).

3. Results and discussion

During the injection of the sulfate-CO_2-rich brine through a fractured limestone core we observed an increase in fracture permeability from 4.5×10^{-13} to 2.8×10^{-11} m^2 (Fig. 2).

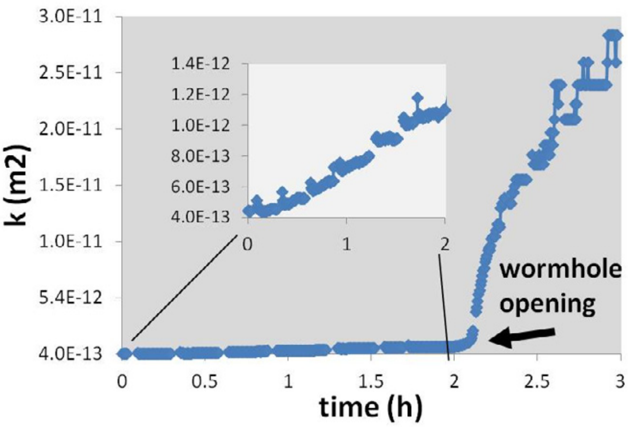

Fig. 2. Variation of fracture permeability with time in a limestone core. The flow rate was 5 mL h^{-1}.

As the synthetic brines circulated through the fracture, the fracture permeability initially increased slowly. After about 2 hours, the increase accelerated. This change could be due to a localized dissolution process (wormhole formation) along the core, possibly also involving gypsum precipitation. The change in solution composition along the core with time allows for the calculation of the volumes of calcite dissolved and gypsum precipitated: 0.025 and 0.01 cm^3, respectively. It is observed that the dominant reaction is the dissolution of calcite as the volume involved is larger than the volume of gypsum precipitated. Visual examination of the inlet and outlet of the cores showed the existence of a wormhole in which needle-like gypsum crystals are clearly visible (Fig. 3).

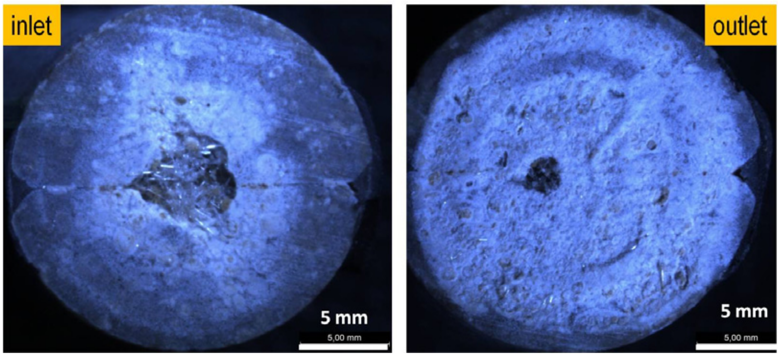

Fig. 3. Frontal views of inlet and outlet of a limestone core. Brine circulated through the fractured core at 5 mL h^{-1}.

X-ray microtomography (mCT) examination of the reacted cores is under way to confirm calcite dissolution (and gypsum/anhydrite precipitation) along the fracture resulting in the development of preferential pathways (wormholes) responsible for the rapid increase in permeability.

Regarding sandstone, initial fracture permeability was found to be ~ 4.7×10^{-12} m^2 (Fig. 4). As the brine circulated through the core, permeability also increased with time. Nonetheless, this increase was not continuous (Fig. 4).

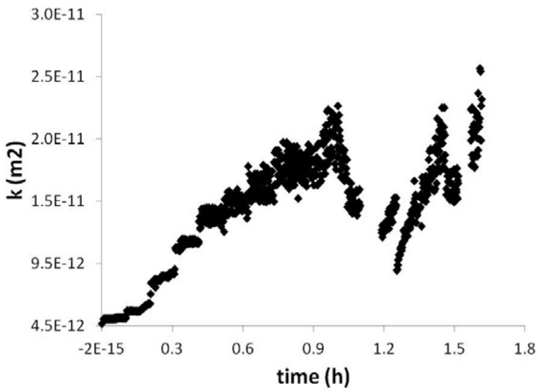

Fig. 4. Variation of fracture permeability with time in a sandstone core. The flow rate was 60 mL h^{-1}.

This behavior could be associated to the movement of quartz grains along the facture as calcite cement dissolved. Variation in solution chemical composition showed that calcite dissolved (calcium excess) but gypsum precipitation was not apparent. Fig. 5 shows the frontal view of the outlet of the column. X-ray microtomography (mCT) examinations of the reacted cores are also under way and are expected to reveal if calcite dissolution (and gypsum/anhydrite precipitation) along the fracture could create preferential pathways (wormholes).

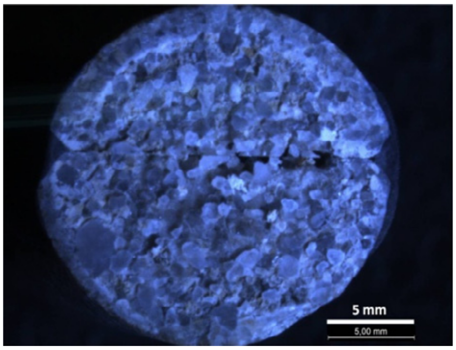

Fig. 5. Frontal view of the outlet of a sandstone core. Brine circulated through the fractured core at 60 mL h^{-1}.

4. Summary

The percolation experiments with mechanically fractured cores showed the capacity of the sulfate-CO_2-rich brines, under pCO2 supercritical conditions, to significantly modify the initial fracture permeability. In each experiment, the permeability increased due to calcite dissolution. Gypsum (or anhydrite) clearly precipitated during the experiment with the limestone sample. Nevertheless, sulfate mineral precipitation could not maintain the initial permeability. During the experiment with the sandstone sample, we also characterized a permeability increase due to calcite dissolution. We observed that the increase in permeability during this experiment was fast from the very beginning of the experiment, unlike the experiment with limestone, which showed an initial period with a very slow increase in permeability. The higher flow rate in the sandstone experiment could possibly explain this behavior (faster calcite dissolution). These experiments clearly show the key role of the local flow rate in dissolution and precipitation processes and the consequences on physical parameters (such as permeability).

Acknowledgements

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