Impact of structural parameters on dissolution processes and the joint evolution of multiphase flow, transport and geochemical parameters in porous rocks

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1 Introduction

Groundwater flow in most consolidated rock aquifers occurs though discrete openings, i.e. fractures, and only to a small extent in the pore network of the rock matrix. The migration of solutes and solvents in fractured rock aquifers is therefore determined by the relative contribution of advective flow compared to matrix diffusion transverse to the flow direction, resulting in retardation of the solute.

The dissolution and precipitation processes not only change the chemistry of the rocks, but also their physical properties such as porosity, permeability, effective diffusivity, tortuosity, reactive surface area, etc. In reactive systems, the pore network is arguably the most important physical characteristic of a rock because it provides pathways for water flow or infiltration and solute transport. The permeability and diffusivity of porous media are functions of the geometry of the pore network that is described in terms of the total porosity, tortuosity, pore throat size, and pore/mineral interfacial area. Chemical reactions can induce changes in the pore network geometry and can therefore change rates of mineral reaction.

Very few published studies evaluate the transport properties changes (porosity, permeability, pore size distribution, diffusion coefficient) due to fluid-rock interactions.

Here we report experimental results from the injection of acidic fluid into limestone core samples of 25.4 mm diameter, 12.5 to 25.4 mm length. Experiments were realized at room temperature. Before and after each acidic rock attack, we measure the sample porosity, the diffusion coefficient and the pore size distribution. We also used XMT images to characterize the pore network changes and to measure the same previous different parameters (porosity, tortuosity, connectivity). We studied two different limestone samples: one composed of 73% of calcite and 27% of quartz, and the second one of 100% of dolomite. Experiments were realized at room temperature. During percolation experiments, the permeability changes are recorded and chemical samples taken to evaluate calcite dissolution and gypsum precipitation.

2 Results

Very few published studies evaluate the transport properties changes (porosity, permeability, pore size distribution, diffusion coefficient) due to fluid-rock interactions (dissolution and/or precipitation). Several dissolution/precipitation-characterization cycles are performed on each sample in order to study the evolution and relation of the different parameters.

These experiments show different dissolution regimes depending of the fluid acidity and of the limestone sample.

Two different rocks have been used for the flow-through experiments. The blanca sample is 100% of dolomite whereas the Euville sample is 73% of calcite and 27% of quartz. Two solutions have been injected through two blanca samples and two Euville samples. Through Euville 5 and Blanca 5 samples, a HAc buffer pH 5.0, 10 mM strenght, equilib. $CaSO4$ solution has been injected. Through Euville 4 and Blanca 8 samples, the same solution have been injected but at pH 4.0. For the four experiences, the flow rate was constant and equal to 10 mL/min.

In Figure 1, we can observe the variation of the Ca, Mg and S concentration for experiments Blanca5 and 8 and Euville 4 and 5. The positive ΔMg concentration indicates dolomite dissolution during Blanca samples percolation whatever the pH was, whereas for Euville samples, we can suggest a calcite dissolution experiments due to the positive ΔCa concentration. For the four experiences, the ΔS concentration is negative indicating a S-rich mineral precipitation. We also can observe in Figure 1, that dissolution process is more important (higher Mg and Ca in the outlet fluid) at lower pH but with similar precipitation. Nevertheless, if we compare the results between dolomite and calcite-rich samples, we can see that gypsum precipitation is higher with dolomite than with calcite.

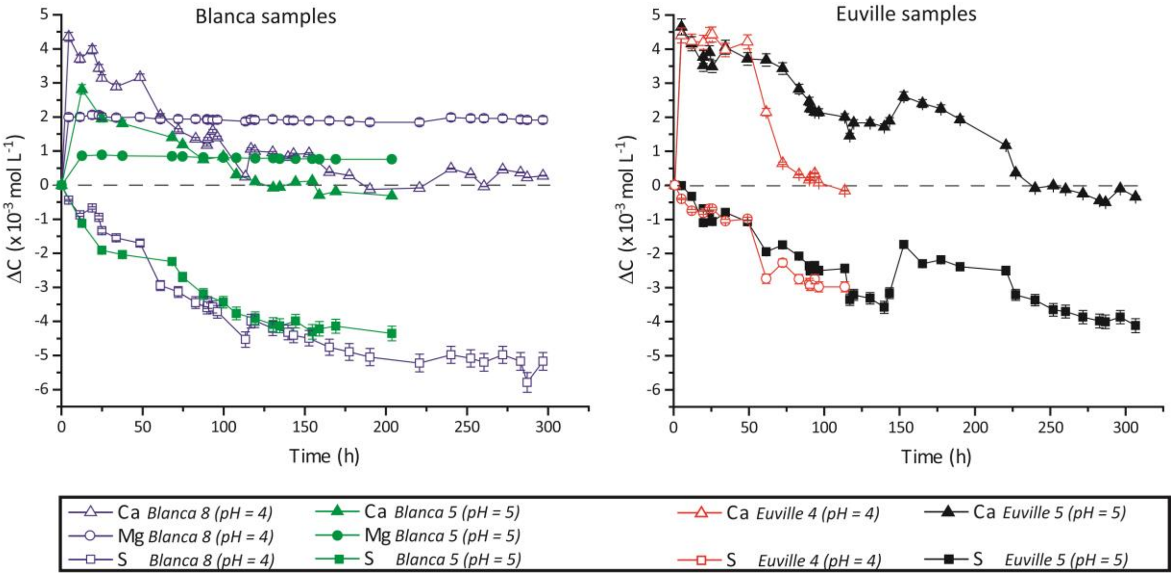


Figure 1: Variation of the Ca, Mg and S concentrations during four different flow-through experiments.

About the permeability change due to these dissolution and precipitation experiments, we can observe in Figure 2, that for Blanca samples, permeability remains quite constant all along the dissolution experiments, whereas for Euville samples, permeability increases suddenly to very high values. Moreover, we can see that the permeability increase is faster for the lowest pH.

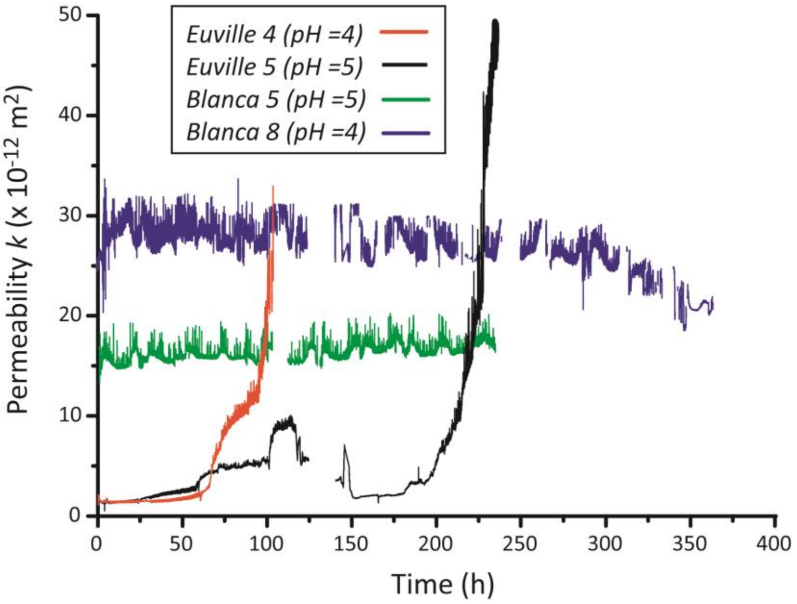


Figure 2: Permeability change during Euville 4 and 5 and Blanca 4 and 8 experiences.

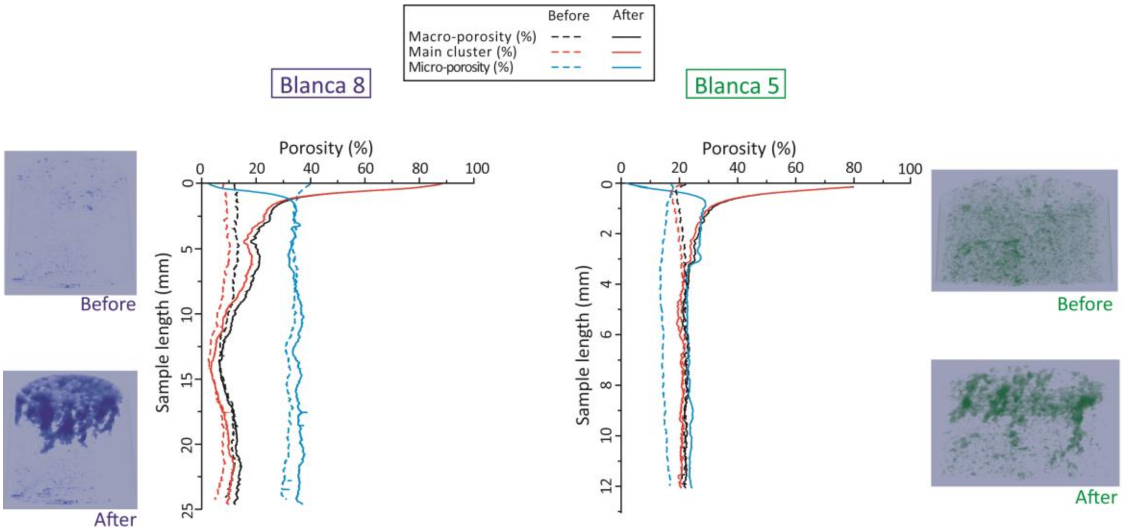


Figure 3: Porosity change along the core samples before and after the percolation experiments for samples Blanca 4 and 8.

We can observe in Figure 3 that during the percolation experiments through samples Blanca, the porosity increase is localized near the sample inlet. Wormholes were formed but did not break through. The macro-porosity increases in the inlet part of the samples where the wormholes are formed. The micro-porosity decreases where the wormholes are developed and increases in the sample remains. XMT images allow us to conclude that even if the porosity is increasing during these experiments, the permeability remains constant due to the fact that the wormhole formed here never breakthrough.

During experiments performed on Euville samples, wormholes are formed and they clearly breakthrough. The permeability was constant up to *t* = 50h and then started to increase. For Euville 5 the permeability started to increase at the same time than Euville 4 and then decreased before increased again around *t* = 200 h. The pH and Ca concentration have the same trend as the permeability curve. One main wormhole was formed in each sample and breakthrough (permeability increase), see Figure 4. The macro-porosity increases all along the sample due to the wormhole formation (more in the inlet part where secondary wormholes are formed). The micro-porosity decreases where various wormholes are developed and increases along the main wormhole.

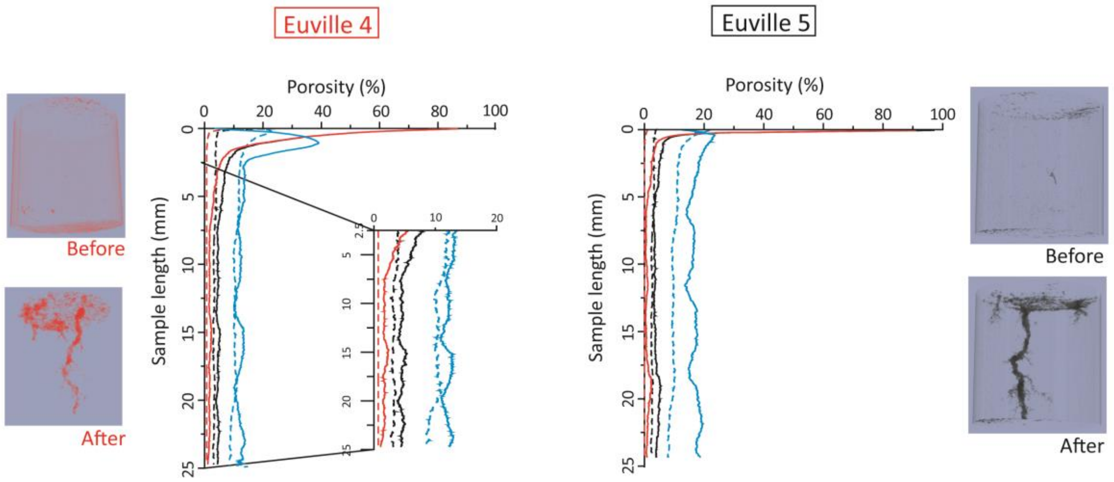
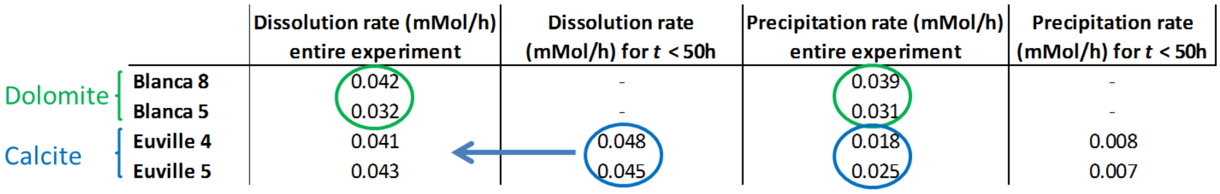


Figure 4: Porosity change along the core samples before and after the percolation experiments for samples Euville 4 and 5.

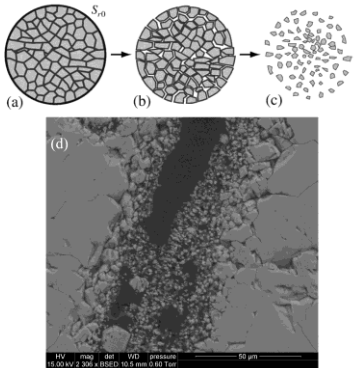
3 Conclusions

- Mineral influence and pH control
    - Calcite dissolution rate is higher than the dolomite one for t < 50h.
    - After wormhole breakthrough the calcite dissolution rate decreases. This decrease is higher for low pH.
    - Whatever the mineral, the dissolution rate is higher for low pH.
    - Gypsum precipitation rate is higher for dolomite than for calcite.



		Dissolution rate (mMol/h) entire experiment	Dissolution rate (mMol/h) for *t* < 50h	Precipitation rate (mMol/h) entire experiment	Precipitation rate (mMol/h) for *t* < 50h
Dolomite	**Blanca 8**	0.042	-	0.039	-
	Blanca 5	0.032	-	0.031	-
Calcite	**Euville 4**	0.041	0.048	0.018	0.008
	Euville 5	0.043	0.045	0.025	0.007

- Structure control



- Role of the micro-porosity on wormhole formation (main wormhole in Euville samples with high micro-porosity content).
- For the same water solution and flow rate, more homogeneous dissolution in Blanca samples than Euville samples.
- Dissolution process first induces micro-porosity increase and then macro-porosity (sugar model, Luquot etal, 2013).

4 References where these results have been presented

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