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# Changes in hydrodynamic, structural and geochemical properties in carbonate rock samples due to reactive transport

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## Abstract

Reactive transport plays an important role in the development of a wide range of both anthropic and natural processes affecting geological media. To predict the consequences of reactive transport processes on structural and hydrodynamic properties of a porous media at large time and spatial scales, numerical modeling is a powerful tool. Nevertheless, such models, to be realistic, need geochemical, structural and hydrodynamic data inputs representative of the studied reservoir or material. Here, we present an experimental study coupling traditional laboratory measurements and percolation experiments in order to obtain the parameters that define rock heterogeneity, which can be altered during the percolation of a reactive fluid. In order to validate the experimental methodology and identify the role of the initial heterogeneities on the localization of the reactive transport processes, we used three different limestones with different petrophysical characteristics. We tracked the changes of geochemical, structural and hydrodynamic parameters in these samples induced by the percolation of an acid fluid by measuring, before and after the percolation experiment, petrophysical and hydrodynamic properties of the rocks.

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*Keywords:* reactive transport; percolation experiments; petrophysics, *PeDa* diagram; heterogeneity

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## 1. Introduction

Predict and model the long-term behavior of both natural (e.g. seawater intrusion, geothermal energy production, hydrothermal processes) and anthropogenic triggered processes (e.g. $CO_2$ geological storage, contamination, acid mine drainage) is a tricky environmental issue due to the heterogeneity of geological media. In order to propose some remediation options, it is necessary to understand the dynamics of these processes and determine the

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properties and parameters which control them.

| **Nomenclature** | | | | | |
|---|---|---|---|---|---|
| $Pe$ | Péclet number | $Z$ | electrical resistivity | $D_{eff}$ | effective diffusion coefficient |
| $Da$ | Damköhler number | $\sigma_r$ | rock conductivity | $v_p$ | velocity of compression waves |
| $\phi$ | porosity | $\sigma_f$ | fluid conductivity | $v_s$ | velocity of shear waves |
| $k$ | permeability | $m$ | cementation factor | $G$ | shear modulus |
| | | $F$ | formation factor | $K$ | bulk modulus |
| | | $\tau$ | tortuosity | $E$ | Young modulus |

Several experimental and numerical studies have been performed to predict reactive processes such as dissolution and precipitation under variable thermodynamic, hydrodynamic and geochemical conditions[1-3]. For dissolution processes, in particular in limestone context (oil reservoir, $CO_2$ storage, karst formation …), some authors[4] proposed a classification of the different dissolution patterns depending only on $Pe$ and $Da$ numbers. These dimensionless numbers bring together the transport and reactive rates for a characteristic length. Nevertheless, recent studies[5,6] proved that $Pe$ and $Da$ numbers are not enough to predict the localization of the processes, in particular in strong heterogeneous rocks. Therefore, a fundamental point is to link the role of heterogeneities and the localization of the dissolution and precipitation processes, such as during the development of dissolution patterns. Especially as these reactions may imply changes in the porosity, permeability and pore-throat radius distribution of the repository, which could vary the $CO_2$ storage capacity and injectivity of the reservoir rock[7-9] or even clog the pore space[10] of the rock matrix. Consequently, a detailed characterization is necessary to quantify the changes involved. This can be achieved following an experimental approach that involves the evaluation of the influence of structural and hydrodynamical heterogeneities. Here, we propose a series of flow through experiments injecting acidic solutions of the same composition under various flow rates in rocks (limestones) with different hydrodynamic and structural properties. The goal was to characterize the role of advective and diffusive zones by tracking the evolution of thermo-hydro-mechanical and chemical (THMC) properties when external variables (such as temperature, flow rate, mixing ratios, among others) change.

## 2. Methodology

### 2.1. Rock samples

A total of 15 cylindrical cores of rock belonging to three different types of limestone were characterized. Preliminary analysis have been accomplished to guarantee the absence of fractures or anisotropy and ensure our samples enable us to work on a representative elementary volume (REV) of a rock matrix over which average can be performed and Darcy law used. All the analyzed rock samples have a diameter of 2.5 cm and a length between 1.25 and 5 cm. The first one is an oolitic limestone from the Oolithe Blanche formation (East Paris Basin), also classically named Oolithe Blanche[11,12]. The second rock, named Beauval, is also an oolitic limestone coming from Beaunotte in Dordogne region in France. It is characterized by light beige to grey color with some shells. The third lithotype, named Euville, is a beige to orange crinoid limestone dotted with fine irregular grains[13].

### 2.2. Petrophysical and hydrodynamic measurements

Characterization has been performed by measuring several petrophysical and hydrodynamic parameters on the core samples: i) Porosity measurements were obtained using two different methods: water porosimetry, known as the triple weighing method and helium porosimetry; ii) $\sigma_r$ was obtained by measuring the magnitude of electrical resistivity of the samples. With this value several parameters that describe the structure of the porous media under consideration can be obtained such as: formation factor, tortuosity, and effective diffusion coefficient. $Z$ measurements were done saturating the cores with four waters with different salinities in order to obtain $F$ using the linear regression of the plot of $\sigma_r$ versus $\sigma_f$; iii) Compressional ($v_p$) and shear wave velocities ($v_s$) of the cores have been measured under dry and wet conditions. We then calculate $E$ and then, the potential deformation of the rock. $G$ and $K$ are calculated from the $v_p$ and $v_s$; iv) Permeability is calculated using both gas and water. The gas pressure and the flow rate into the rock sample are used to calculate $k$. Measurements are made when the samples are under some confining pressure. Permeability changes were also obtained by measuring fluid pressure at the inlet and the outlet of the sample using the experimental setup for percolation experiments. The pressure drop across the sample and the flow rate are measured and $k$ is calculated using Darcy's law; v) Pore size distribution was calculated measuring the retention curve of each sample. We used a centrifuge to apply a high gravity field to an initially saturated sample and measure the drained volume at different suction pressures of water during its drainage[14,15].

### 2.3. Experimental setup

We have designed an experimental bench which allows injecting solutions with a predefined composition at controlled flow rate, temperature and pressure conditions. The setup works at a maximum pressure of 15 bar and 60 ºC, and allows injecting acidic solutions through one or two different rock samples at the same time. Three pair of adapted sensors to measure and register these conditions have been installed before and after both percolation cells. The system is composed of five different types of functional modules: a pressurized tank, a dual piston pump, three sensor hubs (with pH and pressure sensors), two reaction/percolation cells with confining pressure and warming jackets, two pressure multipliers, and two differential pressure gauges to measure changes in permeability with high precision. Also, fluid sampling is available in two different parts of the setup in order to measure the fluid composition and track the changes in geochemical parameters.

## 3. Results

Different parameters such as electrical resistivity, porosity, gas permeability and velocity propagation of compressional and shear waves have been measured to obtain the hydrodynamic and structural parameters that define the heterogeneity of each sample under consideration (section 2.1). Parameters obtained as a result of electrical measurements refers to how well connected is the pore network[16] and its grade of complexity while propagation of sonic waves[17], (and derived modulus, $G$ and $K$) gives information about the anisotropy of the samples and also its pore structure. The different parameters are presented in Table 1. Taking into account these groups of parameters and the relationships between them, their influences on the development of dissolution patterns has been analyzed.

Table 1. Average overall parameters calculated for the different samples of various lengths

| Name | $m$ | $D_{eff}\,(m^2s^{-1})$ | $F$ | $\tau$ (Archie) | $\phi$ (-) | $k\,(m^2)$ | $v_p\,(m/s)$ | $v_s\,(m/s)$ | $G$ (GPa) | $K$ (GPa) |
|---|---|---|---|---|---|---|---|---|---|---|
| Beauval | 2,15 | 1,08E-10 | 46.55 | 7,87 | 0.16 | 8.5E-16 | 4760 | 2190 | 13.60 | 43.77 |
| Euville | 2,10 | 2,72E-10 | 21.40 | 5,20 | 0.24 | 1.82E-14 | 2730 | 1540 | 6.47 | 11.50 |
| Oolithe Blanche | 1,92 | 9,75E-11 | 52.50 | 6,67 | 0.12 | 3.69E-15 | 4110 | 2400 | 16.67 | 41.85 |

Samples belonging to Beauval lithotype present the highest $m$ values, of around 2.15 which correspond to the classic values for carbonates, typically from 1.8 to 2.2[19]. The diffusion coefficient is the lowest with about $1{,}08\cdot10^{-10}$ $m^2s^{-1}$, whereas the porosity is not the lowest one. This indicates that the effective diffusion coefficient is influenced by the high cementation factor value and denotes a strong structure heterogeneity and complexity. Indeed, the tortuosity is 7.87, which is the highest of the three lithotypes attesting to the rock structure complexity and connectivity. Consequently, even if the porosity is reasonable (16%), the permeability presents values close to $8.5\cdot10^{-16}$ $m^2$ which is the lowest one of the three different limestone samples. Nevertheless, parameters derived from the measurement of the sonic waves are 4760 m/s for the $v_p$ and 2190 for $v_s$, which are the characteristic ones for carbonates[18] and indicate large pores diameters as confirmed by the retention curve measurements. Rocks from Euville lithotype present $m$ values of 2.10, which are also in accordance with the common values reported for carbonates. Diffusion coefficient is about $2.72\cdot10^{-10}$ $m^2s^{-1}$, in agreement with the high porosity of 24% (the highest one). Moreover, tortuosity values are the lowest calculated (5.20), which is also congruent with the high diffusion coefficient. According to $\tau$ values, calculated, $F$ is around 21.40 and it corresponds to the lowest of the studied rocks, which can be justified by its higher porosity (24%), and highest permeability ($1.82\cdot10^{-14}$ $m^2$). Data measured for $v_p$ and $v_s$ are the lowest, with values of 2730 and 1540 m/s respectively, in contrast to other reports in the literature[18], although its composition analysed by DRX reveals 99% of calcite[13]. Oolithe Blanche presents a cementation factor of 1.92, which is the lowest, and also a low $D_{eff}$ of $9.75\cdot10^{-11}$ $m^2s^{-1}$. Formation factor of 52.50 is the highest of the whole studied rocks, and is directly related with its lower porosity (12%). A tortuosity of 6.67 has been the intermediate value obtained in comparison with the other lithotypes studied, and corresponds with the intermediate permeability values of $3.69\cdot10^{-15}$ $m^2$. Conversely, this intermediate $k$, is unexpected as the porosity is the lowest one. This can be related with the large pore size distribution obtained with the measurement of the retention curves. Values for $v_p$ and $v_s$ sonic waves are about 4110 m/s and 2400 m/s respectively, which are reported as classic values for carbonates. Based on the literature[20] and the full rock characterization performed here on these three different lithotypes, dissolution process is expected during the acidic fluid percolation experiments whatever the flowrate and the thermodynamic conditions. More especially, we can expect for a same flow rate a more heterogeneous dissolution process in Beauval samples due to the highest tortuosity and permeability and the lowest pore size diameters.

## 4. Conclusions

To better understand the role of local heterogeneity and, in particular, pore morphology and connectivity changes in the rock matrix during dissolution and precipitation of limestones when they enter in contact with acid brine, we proposed a methodology that consists in three main steps. First, perform a complete characterization of the limestone samples belonging to different lithotypes, second, inject an acid brine into rocks under controlled conditions (flow rate, P and T) and third, measure again the same petrophysical parameters quantified before percolation experiments and compare the different trends in variations. The characterization process highlighted several differences between samples that evolved in a different manner after performing percolation experiments. Depending on the structural and hydrodynamic parameters that define rock structure, different dissolution and precipitation processes can be localized (heterogeneous dissolution) and trigger different various parameters changes and relationships between them.

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