INTRODUCTION

CO2 sequestration in deep geological formation seems to be a good solution for minimizing CO2 emissions in the atmosphere. In the vicinity of the injection well, scCO2 will dissolve in the brine and produce low pH solution favouring dissolution of carbonate and to a less extent silicate minerals. Consequently, important modifications of the rock properties (hydrodynamical and mechanical) are expected. Characterizing and modeling these mechanisms is essential for predicting short- and long-term behaviour.

We present results of six percolation experiments which reproduced in situ CO2 injection into two types of oolithic limestone (one with macro-porosity and an only percolating cluster (experiments D1, D2, D3 and D4) and the other one composed of micro- and macro-porosity without an initial percolating cluster (experiments Port1 and Port2)) for different values of Damköhler number (ie. different partial pressure of CO2). X-ray microtomography (XMT), using ID19 at ESRF, is used to characterize, from pore scale to Darcy scale, the changes in the structural properties induced by the percolation of the CO2-rich brine. Coupling imaging techniques with sample scale measurements of the time-resolved permeability and chemical fluxes, allows determining i) the change in the chemical and physical parameters of the sample induced by the dissolution processes and ii) the role of each phase in the formation of the observed preferential flow path.

METHODOLOGY - EXPERIMENTAL CONDITIONS

The methodology combines chemical analysis of the fluid (by ICP-AES) and continuous measurements of sample permeability using the Darcy law. The rock-samples are an oolithic Mg-richcalcite from the Montpellier formation of the Middle Jurassic age (Paris Basin, sample D) and from Alcoaça (Portugal, sample Port).

We consider that chemical alteration of the sample modifies its mechanical and hydraulic properties. Chemical modification is quantified using the Damköhler number,

\[ \alpha = \frac{P_{\text{CO}_2}}{K_{\text{D}}} \]

where \( P_{\text{CO}_2} \) is the partial pressure of CO2 and \( K_{\text{D}} \) is the solubility constant of CO2 in brine (in our case, \( 10^{-3} \) Mpa).

\( \alpha \) is a measure of the degree of chemical alteration. For \( \alpha \approx 1 \), the sample is considered to be in the chemical equilibrium state. For \( \alpha < 1 \), the sample is under chemical alteration, and for \( \alpha > 1 \), the sample is considered to be in the chemical disequilibrium state.

\[ \beta = 1 - \frac{P_{\text{CO}_2}}{P_{\text{CO}_2}^*} \]

where \( P_{\text{CO}_2}^* \) is the partial pressure of CO2 at the chemical equilibrium state. \( \beta \) is a measure of the degree of hydraulic alteration.

\( \beta = 1 \) implies that the sample is in the hydraulic equilibrium state, \( \beta < 1 \) implies that the sample is under hydraulic alteration, and \( \beta > 1 \) implies that the sample is in the hydraulic disequilibrium state.

\[ \gamma = \frac{P_{\text{CO}_2}}{P_{\text{CO}_2}^*} \]

where \( P_{\text{CO}_2}^* \) is the partial pressure of CO2 at the initial state.

\[ \delta = 1 - \frac{K_{\text{D}}}{K_{\text{D}}^*} \]

where \( K_{\text{D}}^* \) is the solubility constant of CO2 in brine at initial state.

\[ \epsilon = \alpha \cdot \beta \cdot \gamma \cdot \delta \]

where \( \epsilon \) is the degree of chemical and hydraulic alteration.

In “D” samples, the initial pore diameters (highlighted here by the chord length function) are larger than those in “Port” samples. During wormhole formation, the chord length function displays higher pore size diameters along \( z \) after experiment than before. The k-\( \phi \) relationship show high n value for experiment D1, D4 and Port2 which display dominant wormhole formation during these experiments. Nevertheless, these three experiments were realized with three different chemical solutions with pH ranging from 3.21 to 3.52.

Experiment D2 was carried out with a pH solution of 3.51 but the n value coefficient is lower and a ramified wormhole was characterized during these dissolution experiment as the experiment Port2 which injected pH solution was 4.38.

Experiments D3 displays more homogenous dissolution with a pH of 4.02.

The porosity along the flow direction increase more at the inlet of the sample during wormhole formation (D1, D2, D4, Port1 and Port2).

For experiment D1, where heterogeneous dissolution is observed, the changes in permeability are due to changes in the hydraulic radius, while for experiment D3, where dissolution is homogenous, the increase of permeability is only due to the decrease of the tortuosity of the porous media.

Finally, for experiment D2 and Port2, \( \alpha \approx 1 \), thus the change in the effective hydraulic radius and the tortuosity during the dissolution control the permeability changes.

For experiment D4, as during experiment D1 and Port1, dominant wormhole was formed and the permeability changes were linked to hydraulic radius changes.

DISCUSSION

Permeability is controlled by the effective hydraulic radius \( \theta \) and the average length \( \lambda \) of the flow paths within the connected pore cluster.

The hydraulic radius is defined as \( \theta = B_{\text{eff}} (\phi - \phi)^n \) depending of porosity change.

Defining the tortuosity \( \epsilon = \lambda / \L \), its value is often related to porosity by the empirical relationship \( \epsilon = 0.5 (1 - \phi) \cdot \theta \).

\[ \log \left( \frac{1}{\epsilon} \right) = \log \left( \frac{B_{\text{eff}}}{B_{\text{eff}}^*} \right) + \alpha \log (\phi - \phi) + \beta \log (\phi - \phi) \]

and \( n = \alpha + \beta \)

For experiment D1, where heterogeneous dissolution is observed, the changes in permeability are due to changes in the hydraulic radius, while for experiment D3, where dissolution is homogenous, the increase of permeability is only due to the decrease of the tortuosity of the porous media.

For experiment D2 and Port2, \( \alpha \approx 1 \), thus the change in the effective hydraulic radius and the tortuosity during the dissolution control the permeability changes.

For experiment D4, as during experiment D1 and Port1, dominant wormhole was formed and the permeability changes were linked to hydraulic radius changes.

CONCLUSION

All experiments show that the sample porosity and permeability increases during CO2 rich-brine injection. For all experiments on samples initially composed of micro- and macro-porosity we observe that the macro-porosity extended at the expense of the micro-porosity (73% and 27% of total porosity respectively). XMT data show that the initial heterogeneity controls the wormhole formations (at constant flow rate). For a same chemical forcing, we characterized different dissolution processes (homogeneous dissolution for D3 and Port) depending on the different structure of the two limestone rocks.

Experimental results show that the dissolution process and the mechanical integrity of the porous system are strongly related to the composition and the initial porosity of the samples. CO2 saturation is a key parameter determining the dissolution process and the mechanical integrity of the porous system.