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Impact of CO₂-induced geochemical reactions on the mechanical integrity of carbonate rocks

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Abstract

In a CO₂ storage site, carbonate rocks might be good reservoir rocks or good seals depending on their porosity and permeability. However, these properties may change in time due to deformation processes related to CO₂ injections and/or withdraws. In this pilot study, we investigate at the laboratory scale the influence of CO₂-induced geochemical reactions on the mechanical integrity of carbonate rocks. To achieve this target, we have performed an experimental HP-HT test on brine saturated oolitic limestone samples that were exposed to 230 bar CO₂ pressure and 37.5°C reaction temperature (supercritical conditions) for a period of 2 weeks. Although changes in fluid chemistry have been identified via ICP-OES analysis, we have observed no particular differences in terms of ooids and cement deformation and/or calcite dissolution when comparing ESEM images of pre- and post-treatment samples. We are currently performing more experiments under different conditions (particularly longer exposure and higher brine-rock ratios that can be linked to higher dissolution of calcite) in order to better understand the dominant CO₂ sequestration mechanisms in oolitic limestone-containing reservoirs.

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Keywords: high pressure-high temperature tests; CO₂; brine; limestone; mechanical integrity

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1. Introduction

Climate change due to human use of fossil fuels leads to additional CO₂ emissions. CCS has a key role to play in curbing CO₂ emissions from thermal-power generation and industrial processes alongside renewables, energy efficiency, nuclear and other mitigation options [1]. However, CO₂ storage can be regarded as a key challenge for a timely CCS deployment to substantially reduce carbon emissions. Up to the present, a number of industrial scale and pilot CO₂ storage projects have been operating worldwide [2, 3]. The idea behind subsurface storage is to inject CO₂ into deep (> 800m) suitable geological formations; CO₂ enters the host rock pore space initially occupied by one or more fluids. Its fate can then follow several possible paths, depending on specific circumstances: for example, CO₂ can migrate upwards as a separate phase, due to buoyancy and becomes physically trapped; alternatively, it can dissolve in the *in situ* fluids, leading to changes in pH and redox states, along with changed density. These changes could lead to fluid motion, or to *in situ* precipitations of solid carbon-bearing minerals, along complex process pathways[4, 5].

Nomenclature

CO ₂	Carbon dioxide
CCS	Carbon Capture and Storage
HP-HT test	High Pressure-High Temperature test
ESEM	Environmental Scanning Electron Microscopy
BSE imaging	Back-Scattered Electron imaging
EDX analysis	Energy-Dispersive X-Ray Spectroscopy analysis
GSE analysis	Gaseous Secondary Electron analysis
ICP-OES	Inductively Coupled Plasma Optical Emission Spectrometry

A number of operational, monitoring and abandoned wells might exist in the storage site. CO₂ is likely to affect the wellbore cement integrity by altering (weakening) the cement properties [6-8], which could potentially lead to CO₂ leakage along the wellbore track. Furthermore, CO₂ injections into the reservoir or leakage from wells could induce minor local seismicity [9] even when the storage site is far from any recognised seismically active zone. Local stress changes, due to the adding chemical reactions to the pre-existing thermo-mechanical loading of the reservoir could create new fractures, further open existing fractures or re-activate pre-existing faults that might be distant from the injection well either within the host rock or in the overlying sealing cap rocks. CO₂ leakage through networks of fractures, faults and wells could significantly enhance any matrix permeability and then become a critical issue affecting long-term storage efficiency and safety.

This pilot study aims at gaining insights into how the physical and petrophysical properties of brine-saturated carbonate rock systems change due to CO₂ injection, with implications for places where carbonate rocks – depending on their porosity and permeability - form either the cap rock or the host rock of the storage site. In particular, we are interested in the influence of CO₂-induced geochemical reactions on the mechanical integrity of an oolitic limestone, which is predominately calcium carbonate, being subjected to typical reservoir conditions at the laboratory scale. To achieve this target, we performed a CO₂ HP-HT test on brine saturated samples, to identify changes in the fluid chemistry and the limestone mineralogy upon the completion of each test. By preparing pre- and post-treatment thin sections from regions close to the sample edges we aim at identifying possible deformation micro-processes and mineral changes that could occur due to the thermo-chemo-mechanical coupling.

2. Material and Experimental set-up

The study material is an oolitic limestone from an outcrop on the edge of the Paris Basin, France. It consists of ooids that are either rounded or elliptical with a mean size of 400-600 μm (Fig. 1). Observations of thin sections show that, although there are some very small sporadic pores, the ooids are surrounded by cement - typically filling

most of the between-oid space, which leads to the conclusion that this is a rather low porosity carbonate. However, occasional big pores, apparently where ooids have been removed, can result in local higher porosity.

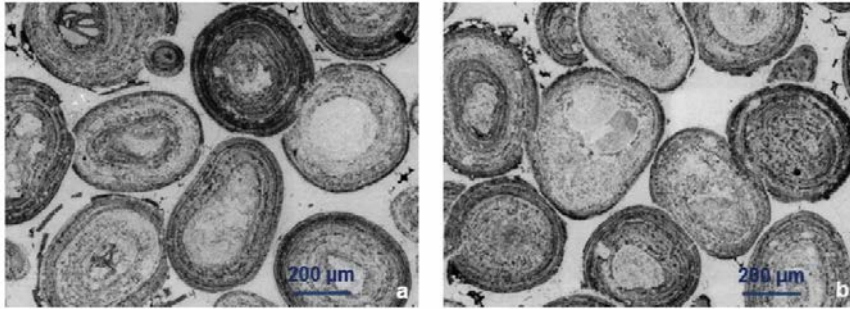


Fig. 1. (a-b) BSE image of a thin section from the oolitic limestone showing the ooids surrounded by cement.

To investigate the effect of CO₂ injection on the mechanical integrity of this particular limestone, a HP-HT test at the laboratory scale (Fig. 2a) was performed. This experimental test was conducted in a custom built 75 mL 316L stainless steel pressure vessel at supercritical (P_{CO₂} = 230 bar) CO₂ pressure, reaction temperature of 37.5°C and residence time of 2 weeks. A polytetrafluoroethene (PTFE) liner was inserted into the body of the reactor to prevent its corrosion under experimental conditions. The limestone sample (42.8 g, Fig. 2b) was submerged in 45.5 mL of a synthetic brine solution (Fig. 2c), which was prepared as an analogue to a natural brine coming from a natural gas well in Youngstown, Ohio [10, 11]. Owing to the complex composition of natural brines, only major ions were considered for the preparation, including K⁺, Mg²⁺, Ca²⁺ and Sr²⁺. Prior to the experiment, an initial brine pH of 6.2 was measured at ambient temperature, which increased to 7.1 upon contact with the submerged limestone rock.

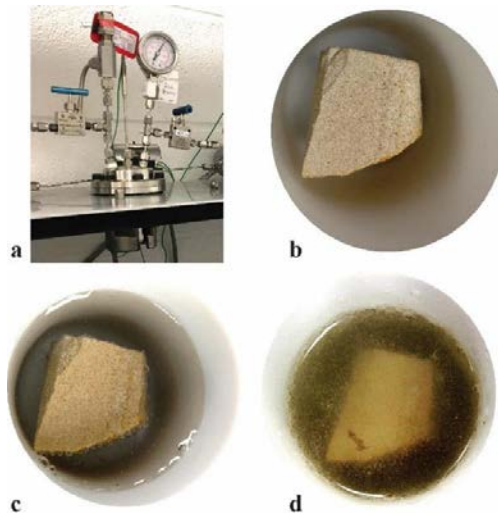


Fig. 2. (a) HP-HT vessel; (b) Oolitic limestone sample before the HP-HT experiment; (c) Oolitic limestone sample submerged in the synthetic brine before the HP-HT experiment; (d) Oolitic limestone sample in carbonated brine after the HP-HT experiment.

The pressurization and heating of the vessel to achieve reaction conditions of 230 bar and 37.5°C was carried out stepwise, so as to avoid any potential deformation that could be linked to thermal shock of the limestone. Therefore,

initially, CO₂ pressure that was supplied by means of a syringe pump (ISCO Corp.) was increased from atmospheric to 50 bar. Then, reaction temperature was increased in steps of 5°C from 21°C (room temperature) to 37.5°C and afterwards, it was kept constant during the whole experiment. Finally, CO₂ pressure was increased from 50 to 230 bar and it was kept constant until the end of the experiment. Temperature was supplied by a heating jacket and maintained constant by a temperature controller.

At the end of the experiment, the pressure and temperature were gradually lowered back to atmospheric conditions and the carbonated brine solution-limestone mixture (Fig. 2d) was vacuum-filtrated to separate the solids from the aqueous solution. The pH of the degassed brine was also measured (6.6).

Two different methods have been used to analyze the influence of supercritical CO₂ on the mechanical integrity of this limestone: a. ICP-OES analysis on starting and reacted brine solutions, and; b. ESEM imaging of thin sections coming from the oolitic limestone sample after the thermo-chemo-mechanical loading. To identify any potential changes due to CO₂ injection, thin sections were also prepared from samples that didn't undergo any laboratory scale loading. All micro-scale observations were made in regions 1-3 mm from the sample edges (i.e. places from where thin sections were cut).

3. Results and discussion

The brine composition measured by ICP-OES before and after the CO₂-limestone-brine experiment is shown in Table 1. Duplicate measurements were obtained for the composition of the reacted brine. As it can be observed, the main change in the composition of the brine comes from an increased calcium concentration (approximately three times higher than that in the starting brine). This observation suggests that the increased acidity in the reaction system due to CO₂ injection and its subsequent dissolution into the brine has dissolved the limestone (>90% CaCO₃), and CO₂ remained mainly trapped as dissolved aqueous species instead of as mineral carbonates.

Table 1. Composition of initial and reacted brine.

Concentration [ppm]	Ca ²⁺	K ⁺	Mg ²⁺	SO ₄ ²⁻	Sr ²⁺
Target Brine	639	227	69	---	59
Synthetic Brine (before experiment)	682	277	85	15	45
Synthetic Brine (after experiment)	2069	324	90	40	57
Synthetic Brine (after experiment-duplicate)	2096	346	93	44	61

Grain-scale investigations based on thin section observations (ESEM imaging) on the brine-saturated limestone sample after the HP-HT experiment have shown no obvious fractures due to the thermo-chemo-mechanical loading of the sample. Micro-porosity in a few ooids together with occasional big voids in cement between ooids have been identified locally in the post-deformation sample (Fig. 3), however similar observations were made in the pre-laboratory deformed sample. Moreover, a few sporadic fractures along ooids (Fig. 3b) have been identified in both pre- and post-deformation samples.

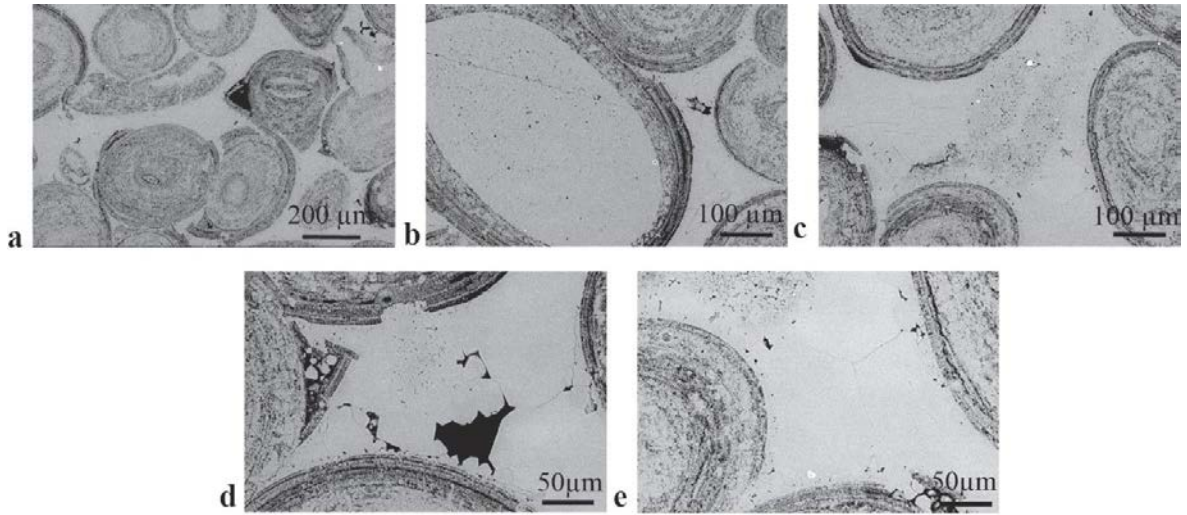


Fig. 3. (a-e) BSE images of different scale focusing on the ooids, the cement surrounding the ooids and the pores.

EDX maps on thin sections from this carbonate before the HP-HT test (Fig. 4a-4d) and after the HP-HT test have both revealed that a. calcium exists within the ooids and the cement; b. carbon has a higher concentration in the concentric laminae of the ooids, which could be due to organic matter or resin impregnation.

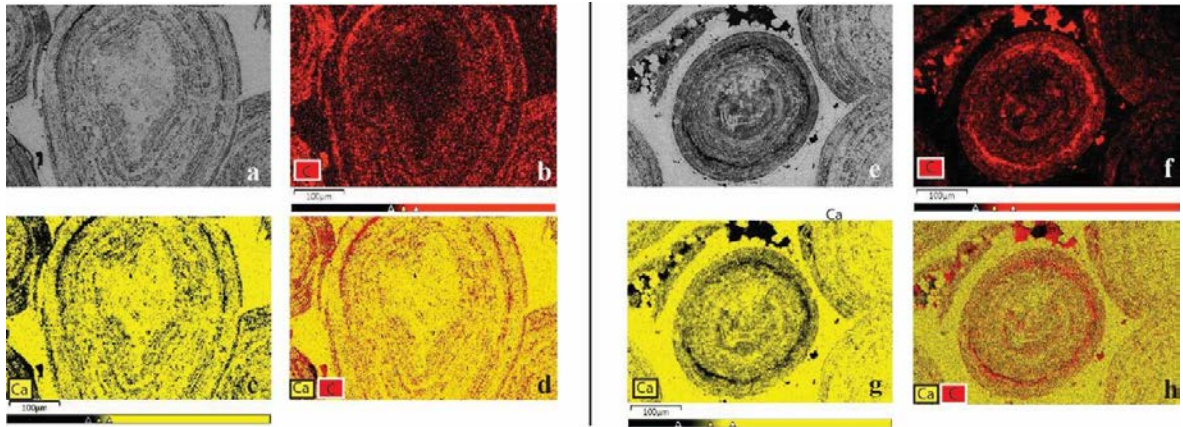


Fig. 4. (a) BSE image focusing on an ooid from oolitic limestone; (b) EDX maps showing the distribution of C; (c) EDX maps showing the distribution of Ca; (d) C and Ca maps form the same region; (e) BSE image from an ooid after the HP-HT testing; (f) EDX maps showing the distribution of C; (g) EDX maps showing the distortion of Ca; (h) C and Ca maps form the same region.

Calcite cement grew into the pore space from the ooids' margin, as a fine grained radially orientated cement phase, followed by a coarser pore occluding cement. However, calcite is not everywhere well attached to the ooids. Moreover, micro-porosity and pressure solution have been identified within some of the ooids and at their edges, respectively. By comparing EDX images from this limestone before and after the HP-HT test no particular differences related to the thermo-chemo-mechanical deformation could then be identified.

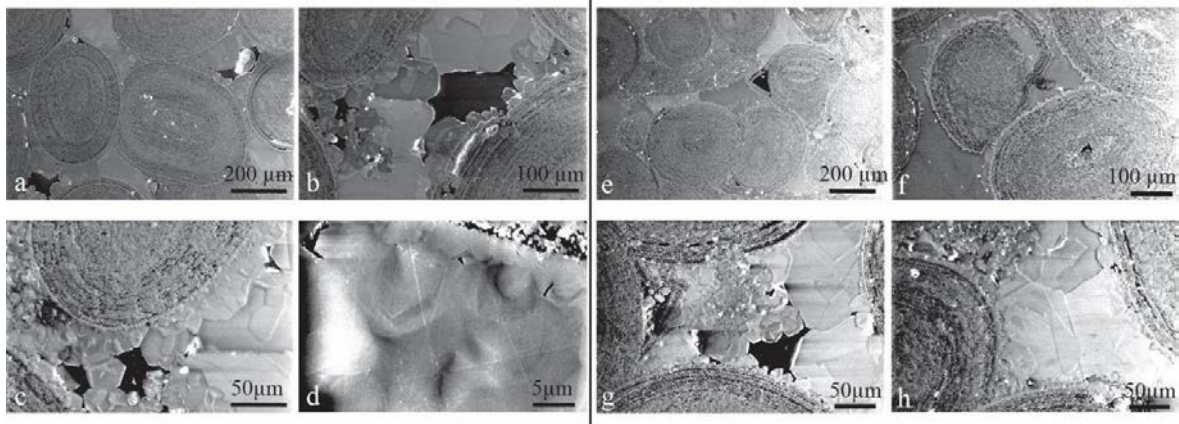


Fig. 5. GSE images from the oolitic limestone before the HP-HT test (a-d) and after the HP-HT test (e-h).

4. Conclusions

We have performed a HP-HT CO₂ test on a brine saturated sample of oolitic limestone under reservoir conditions representative of a potential CO₂ storage site. On the one hand, microstructural observations indicate no actual grain-scale deformation and calcite dissolution due to the CO₂ injection. On the other hand, the increase in concentration of calcium ions in the reacted brine has been linked to dissolution of the limestone, which has possibly taken place along the surface of the sample. Therefore, it can be argued that under the current test conditions (230 bar, 37.5 °C, 2 weeks' exposure) CO₂ does not damage this potential repository rock. Further research on different conditions (particularly longer exposure and higher brine-rock ratios that can be linked with faster dissolution of calcite) is currently underway.

Acknowledgements

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