Carbonate Rock Dissolution under Carbonated Water Injection (CWI)

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ABSTRACT

A set of core-flooding experiments were performed in order to investigate changes in mass, porosity and permeability of dolomite samples due to dissolution and precipitation phenomena occurring during Carbonated Water Injection (CWI). Experiments were carried out under pressure ranging between 7500 and 8500 psi, temperature of 70°C, and flow rate of 2 cm³/min. The core-flooding experimental set-up included two core-holders arranged in series, enabling the recording of differential pressure across each core separately during the tests. X-Ray Computerized Tomography (CT) revealed that the greatest effect of dissolution occurs in the first centimeters from injection point, after which dissolution and precipitation phenomena coexist and porosity tends to remain unchanged. CT data also showed that initial porosity can favor dissolution or precipitation to predominate at pore scale. Differential pressure across dolomite samples were measured using pressure transducers. Results did not show significant changes in samples' permeability in the first core-holder. However, a decrease in permeability was observed in the second core-holder, caused by mineral precipitation.

INTRODUCTION

According to the Earth System Research Laboratory [1], CO_2 concentration in the air has grown 27% from 1965 to 2017, intensifying the greenhouse effect. CO_2 sequestration in geological formations is being considered worldwide as a feasible option to limit the overload of CO_2 emissions. Besides that, CO_2 injection in petroleum reservoirs as an Enhanced Oil Recovery (EOR) method has been showed to increase oil recovery in many studies [2,3,4]. The Brazilian Pre-salt carbonate reservoirs, among the world's most important discoveries over the past decade, has been presenting high content of CO_2 in high pressure conditions (~8500 psi). In this sense, the reinjection of produced CO_2 can be the most attractive option, both environmentally and economically.

Carbonated Water Injection (CWI) has some advantages over other CO_2 injection methods. Due to its density, injected carbonated water moves to lower parts of the reservoir, preventing the formation of bulk-phase CO_2 that will migrate upwards and can lead to CO_2 leakage through seal rock [5]. CWI also leads to a wider CO_2 distribution over the reservoir and can postpone CO_2 breakthrough at production wells [2]. Carbonated water, however, generates carbonic acid (H_2CO_3), which reduces the pH of reservoir fluids. This is particularly important during CWI in carbonate reservoirs, once interactions between carbonated water and host rock will lead to mineral dissolution/precipitation and to

porosity and permeability changes [6,7,8,9,10,11]. Dissolution of carbonate rocks are related with increase in permeability and porosity, while precipitation, with the reduction of these properties [12]. Depending on how the reactive-flow alters rock properties, well injectivity can change severely [13, 14].

Brazilian pre-salt carbonates are highly heterogeneous. Dolomite is a rock type representative of large volumes of the reservoir rock. A small number of experiments are reported in the literature regarding dolomite dissolution under CWI. The experimental procedure used here aimed at mimicking mass transfer as a result of reactive flow at regions near the injection well, and allowing the analysis of porosity and permeability changes in the carbonate rock. In this region, high flow velocity and highly reactive fluid are expected to be present. This paper reports four flow-through experiments in which CO_2-charged brine is pumped at high flow rate through two core-holders at *in situ* conditions of pressure and temperature arranged in series, each one containing a dolomite core plug. X-ray macro tomography imaging is used for the evaluation of porosity at core size level. Pressure drop variations across each of the core plugs were recorded to compute permeability. Chemical analysis of the produced fluids allowed investigation of the dissolution phenomenon. Results focus on the effects of dissolution/precipitation on mass, porosity, and permeability of the rock during CWI and provide a better understanding of conventional petrophysical properties changes during implementation of a CWI project in carbonate reservoirs.

PROCEDURES
Samples
The dolomite samples were gathered from an outcrop belonging to Thornton Formation, from United States. X-ray Diffraction (XRD) technique was used to determine dolomite composition. The XRD technique was done using an X'Pert Philips X-ray Diffractometer, and was performed at the Calibration and Analytical Resources Laboratory, at the University of Campinas. Rock composition was determined to be 100% dolomite – $CaMg(CO_3)_2$. The core plugs had diameter of 3.8 cm, and their properties are presentedon Table 1. Sample mass, effective porosity, and permeability were measured both prior and after reactive flow (except for tests 2 and 3), using a precision scale (Adventurer OHAUS), a gas porosimeter (CoreLab instruments UltraPore 300), and a gas permeabilimeter (CoreLab Instruments Ultra-Perm 500) respectively.

Fluids
Three distinct fluids were used during the experiments: (1) nitrogen, (2) synthetic brine, (3) synthetic brine saturated with CO_2. Nitrogen and synthetic brine are used to saturate samples as part of X-ray tomography procedure. The synthetic brine is chemically balanced with dolomite. Brine saturated with CO_2 is the injection fluid for all tests. To prepare the injection fluid, a stainless steel vessel was filled with deaerated synthetic brine, and then a controlled volume of CO_2 was introduced into the brine. The minimum volume of CO_2 to be mixed with synthetic brine was calculated using a model of CO_2 solubility in sea water [15]. Then, a larger volume of CO_2 was added to brine in order to guarantee 100% of saturation with CO_2 at tests' conditions of temperature and pressure. After that, the carbonated brine was heated to 70°C and pressurized up to test pressure. To ensure brine-

CO_2 mixture, the vessel, which has a free movable sphere inside, was attached to a mechanical device for mixing during 24 hours. During the experiments, carbonated water vessels were kept in vertical position to avoid CO_2 excess volume to be injected along with carbonated water.

Experimental Set-Up

An experimental apparatus was designed to perform CWI in reservoir samples distributed in two core-holders (CH1 and CH2) arranged in series, which enables the recording of differential pressure across each core separately during the test (Figure 1). Each sample was cemented (to fill surface irregularities), wrapped with Teflon tape, aluminum foil, and a heat shrinking film, and then inserted into a rubber to avoid fluid leakage. Confining pressure, in all cases, were set 2000 psi higher than injection pressure. Band heaters connected to temperature controllers were used to keep core-holders and CO_2-saturated brine vessels at constant temperature. A positive-displacement pump was used to inject fluids at continuous flow rate, while a back pressure regulator controlled injection pressure. Fluid sample collection was done at injection system outlet.
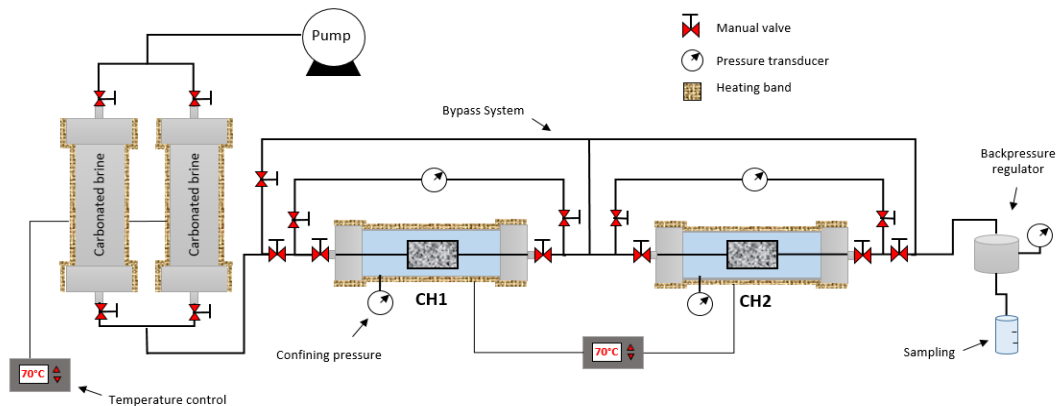

Figure 1. Experimental apparatus.

Experimental procedure

The experiments consisted of the injection of CO_2-saturated brine through core plugs of dolomite at temperature of 70°C. Tests 1, 2, and 3 were performed at the pressure of 8500 psi, while test 4 was carried out at 7500 psi. A constant flow rate of 2 cm^3/min was used in all tests.

Before each core-flooding, both samples were saturated with synthetic brine and pressurized up to test pressure. Synthetic brine flowed first through the bypass and then both core-holders were opened to flow. Once steady-state pressure gradient was stablished across the samples, carbonated brine vessels were opened to flow and bypass system valves were closed. Tests lasted up to 12 hours. The samples were scanned using X-Ray Computerized Tomography (CT) several times during experiment evolution, at a higher frequency in the first two hours. Every CT scanning generated one image for each mm of core length. Absolute porosity was calculated for each image individually, and an average of all image porosity values furnishes the total core porosity [16]. Therefore, porosity

behavior could be analyzed both spatially and along time. For test 2, fluid samples were collected and calcium concentration was obtained using Ion Chromatography (ICS-5000, Thermo Scientific). Differential pressure data registered with both pressure transducers allowed the calculation of core permeability for every second of test through Darcy's law.

RESULTS

Measurements before and after experiments for tests 1 and 4 showed mass reduction in all samples, and mass loss in the CH1 samples was from eight to eleven times greater than in the CH2 ones (Table 1). Effective porosity (measured using the porosimeter) increased 5% in the first samples, while it continued almost unchanged in the second ones. Porosity evolution during reactive flow was obtained for all tests using X-ray Computerized Tomography (CT), and the results are shown on Figure 2, where porosity values are normalized. Overall porosity in CH1 samples tended to remain approximately constant or increase, while the CH2 samples remained constant or decreased. Pressure reduction from 8500 to 7500 psi for test 4 did not change the porosity alteration pattern observed in all tests.

Initial and final porosity distributions along all samples are shown on Figure 3. The greatest increase in porosity (up to 35%) took place within 2 cm from the injection face of CH1 samples, where the phenomenon of dissolution was predominant. CH2 samples porosity tended to remain largely uniform along the cores length. Porosity increase was greater in regions with higher initial porosity, while porosity decrease was greater in regions with lower initial porosity, showing that this phenomenon can be highly influenced by heterogeneities previously present in the dolomite sample. Probably, the sample used in test 3 (CH1) showed a particular characteristic related to mineralogical composition and its degree of consolidation. In fact, each plug sample (CH1) showed a particular behavior in the corresponding tests. That is indicative that dissolution depends on rock heterogeneity as well as on minor changes of the rock mineral composition.

Table 1. Core plugs characteristics before (initial) and after (final) experiments.

Sample	Core Length (cm)	Core Mass (g)		Core Porosity (%)		Core permeability (mD)	
		Initial	Final	Initial	Final	Initial	Final
Test 1 CH1	5.9	161.73	160.4	14.4	15.0	116	58
Test 1 CH2	5.8	160.43	160.27	13.71	13.79	109	85
Test 2 CH1	6.2	166.59	-	16.49	-	403	-
Test 2 CH2	6.4	171.41	-	15.97	-	303	-
Test 3 CH1	5.0	132.63	-	16.84	-	391	-
Test 3 CH2	6.2	167.19	-	15.78	-	315	-
Test 4 CH1	6.4	175.86	174.85	13.43	14.1	119	68
Test 4 CH2	6.1	169.38	169.29	13.79	13.76	122	37

Figure 4 shows calcium concentration in produced fluid against PVs injected during test 2, where the baseline refers to concentration in unaltered brine. Throughout the core-flooding experiment, data remained above the baseline value. Calcium production did not present significant changes after rapidly reaching around 0.04 mol/kg. This is an indicative that dissolution stabilized rather quickly.
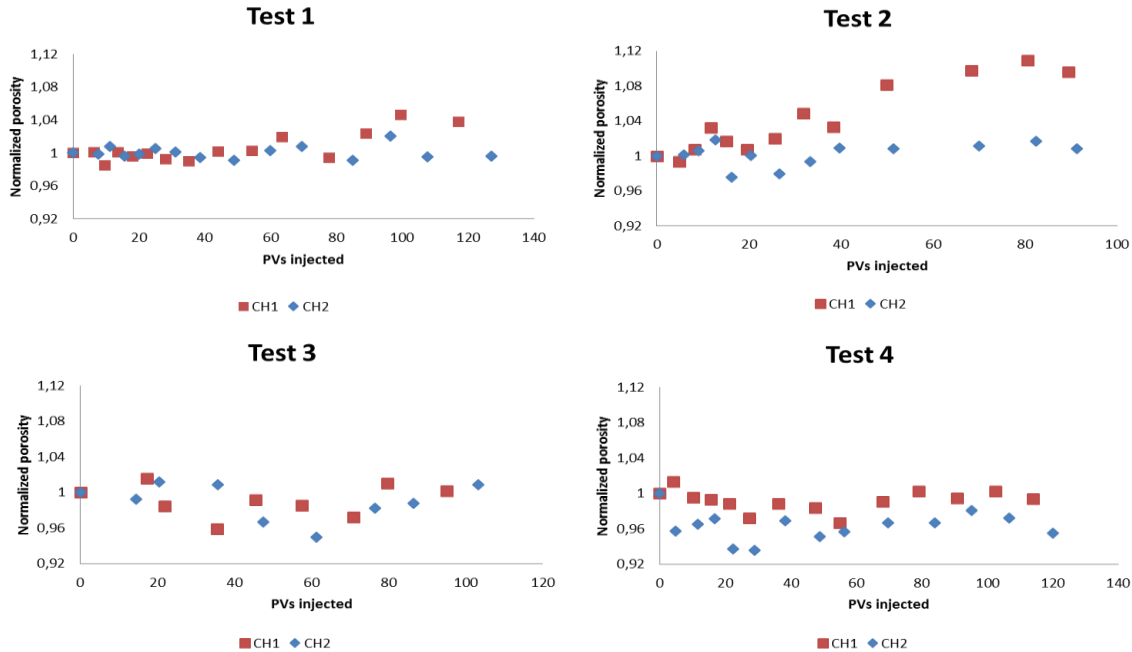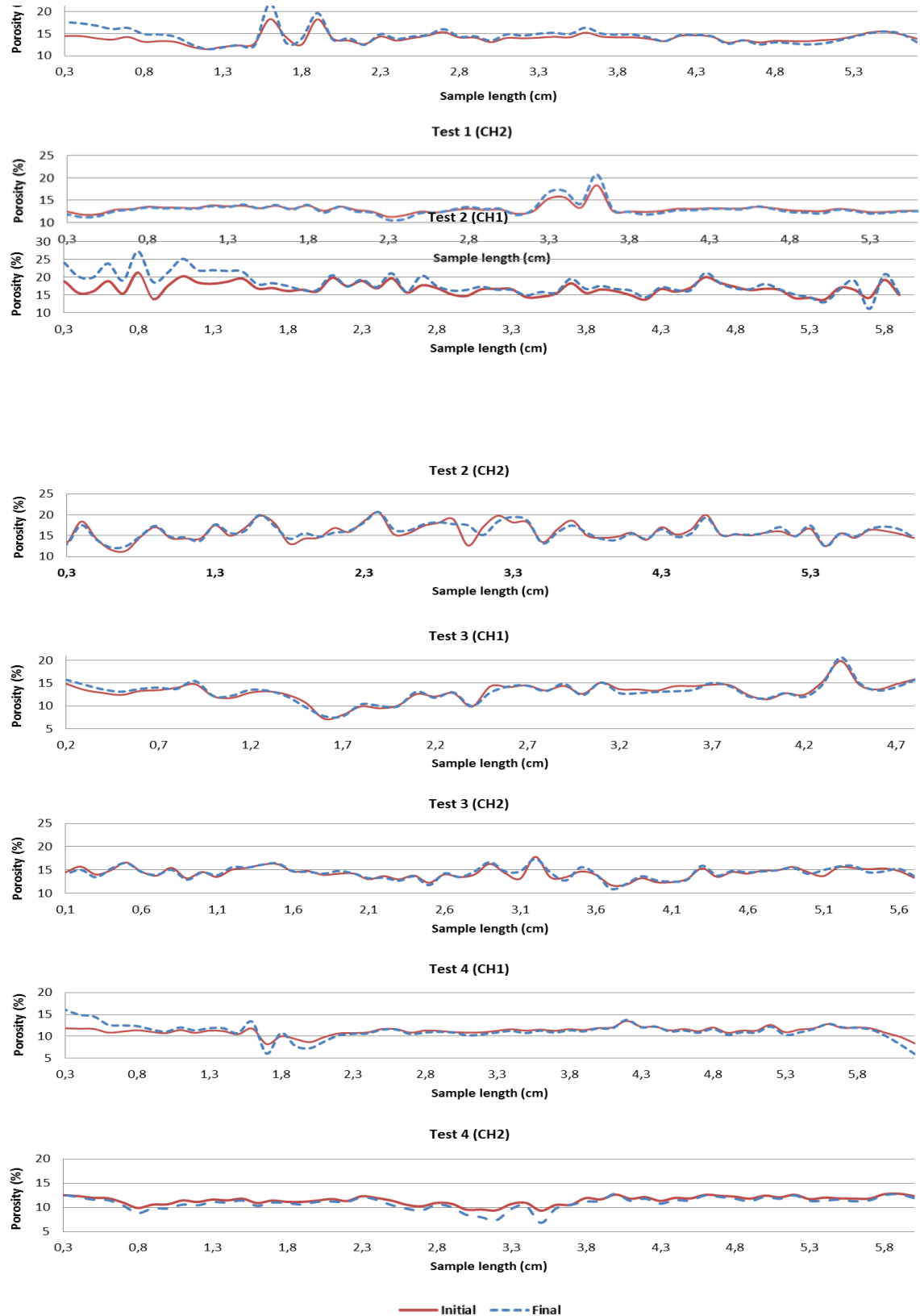

Figure 2. Porosity evolution (normalized) during experiments. Data were obtained with CT.

Measurements in the permeabilimeter showed a permeability reduction that varied from 43% to 50% in the CH1 samples and from 22 to 70% in the CH2 samples (Table 1) for tests 1 and 4. Figure 5 shows permeability data (normalized) obtained from pressure transducers during test 3. Permeability for CH1 sample presented a small decrease in the first PVs injected, and remained unchanged during the rest of the test. A decrease in CH2 sample permeability was observed, mainly during the first 60 pore volumes injected, due to precipitation. It is important to point out that the permeability data obtained from the permeabilimeter (Table 1) are not expected to be the same as the permeability data obtained from pressure transducers during carbonated brine injection (as the ones shown on Figure 4). This is due to differences in effective pressure and in injection fluids between both methods. Furthermore, during apparatus disassembly, the pressure reduction through which the sample goes can have caused mineral precipitation, which can be responsible for permeability decrease indicated by permeabilimeter measurements (Table 1).

Figure 3. Absolute porosity distribution along samples. Data were obtained using CT.

Test 1 (CH2)

Test 2 (CH1)

Test 2 (CH2)

Test 3 (CH1)

Test 3 (CH2)

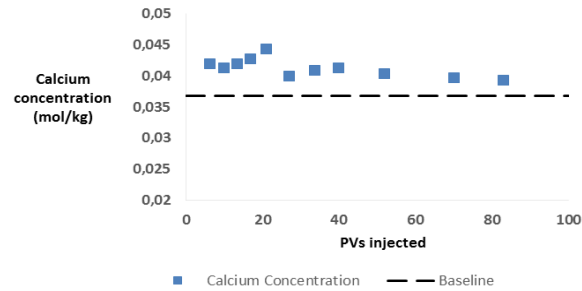Test 4 (CH1)

Test 4 (CH2)

Initial   Final

Figure 4. Calcium concentration in produced water during test 2.
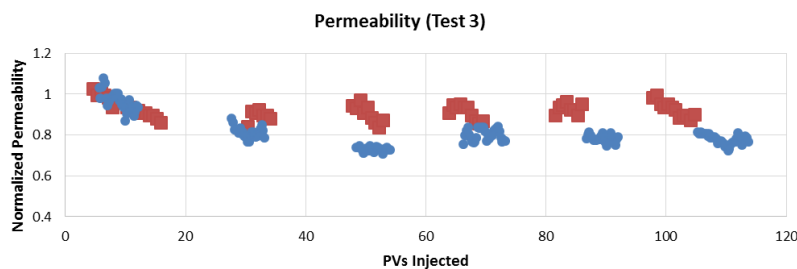The baseline refers to original composition of injected brine.

Figure 5 - Permeability (normalized) evolution during test 3.

DISCUSSIONS

Luhmann *et al*. [11] calculated dolomite porosity evolution under CO_2-charged brine based on mass balance, showing porosity increase in all experiments. Here, the experimental porosity data based on CT shows that overall porosity of dolomite does not always increase during carbonic acid injection due to coexistence of dissolution and precipitation phenomena along the samples. Properties related to porous media, such as surface area and initial porosity, will impact on dissolution and precipitation phenomena. Existing heterogeneities will influence fluid-rock reaction. It can be seen in the results that locations with higher initial porosity will be more likely to be dissolved in comparison with their surroundings, once flow velocity will be lower and fluid will have a longer contact time with pore walls. The opposite trend is seen in regions with lower initial porosity. This is especially important for dolomite due to its low dissolution rate. Higher porosity alterations due to dissolution occurring within the first centimeters of the dolomite sample showed that a small volume of rock was sufficient to bring carbonated brine to chemical equilibrium. In this sense, during CWI into dolomite rock, it is not expected that dissolution effects will be important at regions far away from the injection well. However, after injection fluid breakthrough, pressure decreases could lead the saturated fluid to precipitate, thus reducing permeability around production wells.

CONCLUSIONS

1. Significant increase in dolomite porosity due to carbonic acid dissolution occurs within few centimeters from fluid injection point, after which dissolution and precipitation coexist and porosity tends to remain unchanged.

2. Overall porosity of dolomites can experience increase or decrease near injection well during CWI, while permeability is expected to decrease in the cited region.

3. Porous media structure of dolomite can favor dissolution or precipitation to occur. Regions with relatively higher initial porosity will favor dissolution to preponderate, while precipitation can be induced in sections with lower porosity in relation to their surroundings.

NOMENCLATURE

CH1   Core-holder 1
CH2   Core-holder 2
CO_2 Carbon dioxide
CT   X-Ray Computerized Tomography
CWI   Carbonated Water Injection
H_2CO_3 Carbonic acid
PVs   Pore Volumes
XRD   X-Ray Diffraction

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