LABORATORY STUDY ON CARBONATE ROCKS CHARACTERIZATION AND POROSITY CHANGES DUE TO CO₂ INJECTION

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Received: 10.03.2016 / Revised: 07.06.2016 / Accepted: 09.06.2016 / Published on line: 12.07.2016

ABSTRACT

Enhanced oil recovery methods must be improved continuously to provide higher recovery factors for the new fields under development in a globally competing market. CO₂ injection processes in carbonate rocks involve reactions between acid brine and the rock. These interactions promote petrophysical changes in the rock structure due to calcite dissolution or precipitation. Lab experiments in saturated coquina samples were carried out to better understand the effects on porosity by CO₂ injection. X-ray Photoelectron Spectrometer (XPS) was used to analyze the surface chemistry of the rock sample for elemental composition measurement. X-Ray Micro-CT and Mercury Injection Capillary Pressure (MICP) were carried out to calculate mean porosity in the rock sample. X-Ray scans were run for each pore volume injected. The results show that dissolution should be considered when supercritical CO₂ is injected in the reservoir. This process has relevance for project design, risk analysis, economic evaluation and reservoir behavior forecast.

KEYWORDS

rock characterization; CO₂ injection; reservoir engineering; enhanced oil recovery; chemical reactions

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doi:10.5419/bjpg2016-0009

1. INTRODUCTION

One of the main challenges for reservoir engineering is the disposal of carbon dioxide (CO₂) generated during oil production from CO₂-rich reservoirs. Recent reports on the potential of pre-salt reservoirs mention deposits up to 7,000 meters deep, containing light oil of low acidity and low sulfur content, along with about 3.1 billion tons of carbon dioxide, which occupies about 10% to 15% of the reservoir volume (**Carbon Capture Journal, 2010**). Cost reduction has been constantly discussed for the application of carbon capture and storage (CCS). Carbon dioxide when in contact with other components presents a corrosive characteristic, which leads to an increase in project costs. A common solution presented is the injection of CO₂ into the reservoir with a twofold objective: (1) to improve oil recovery and (2) to reduce emission costs. However, injection of CO₂ into carbonate rocks brings new problems, diverse from those associated with injection of other fluids for oil recovery (**Meyer, 2007**).

In the pre-salt area, oil companies intend to adopt technologies of carbon capture and sequestration on the reservoir itself to reduce emissions of gases that occur during oil extraction. The fluid flow and mass transfer behavior of the injected carbon dioxide in the porous rock saturated with oil is highly relevant for the areas of project design, risk analysis, economic evaluation, and field development strategy.

Regardless of the rock composition, gradual dissolution of CO₂ into the formation water (generally in thermodynamic equilibrium with the rock-forming minerals) leads to a decrease in pH. As a result, the main process involves the dissolution of carbonates and possibly silicates, depending on the kinetics of individual responses. Near the injection well, where the unbalance is greater, the dissolution of solid processes may affect the mechanical properties and fluid dynamic of the rock irreversibly. Specifically, the dissolution leads to an increase in porosity and permeability, as well as to changes in the reactive surface area of the mineral. On the other hand, increased cation concentration produced by carbonate dissolution can supersaturate the fluid ahead in the flow front. In this case, it is expected that precipitation would lead to a decrease in porosity and permeability (**Luquot et al., 2009; Egermann et al., 2005; Andreani et al., 2009; Hoefner & Fogler, 1988**).

The aim of this paper is to characterize and study the effects of CO₂ saturated brine injection in carbonate rocks. The study had an experimental stage with tests involving the co-injection of CO₂ and brine in samples of calcareous rocks. The study focuses on the temporal effects of permeability and porosity of the rock during injection. The experiments will use non-destructive techniques (X-ray Photoelectron Spectrometer, tomography, and micro tomography) and mercury injection capillary pressure (MICP) for rock characterization and to quantify the texture changes in the rock and, eventually, identify the porous sub-systems most affected by the reactions. The X-ray Photoelectron Spectrometer (XPS) analyses were developed at LNNano - Brazilian Nanotechnology National Laboratory, CNPEM/MCTI and the Micro tomography at Petrobras Research and Development Center (CENPES).

2. MATERIALS AND METHODS

2.1 Calcite chemical reactions

The system composed by CO₂(g) – H₂O – CaCO₃ produces, by chemical reactions, the most common acid in natural water systems the carbonic acid. A series of chemical reactions occur in the system (**Al-Shalabia et al., 2014**):

Equations (1) and (2) show the carbonic acids formed by CO₂ dissolution in water where CO₂(g) becomes CO₂(aq) and associates with water molecules. Depending on the formation pH, calcite is affected directly by the formed carbonic acid. The acid is dissociated according to Equations (3) and (4). The calcite dissolution is given by Equation (5), and the summarized effect of calcite dissolution by CO₂ injection can be expressed by Equation (6). It is worth to remind that calcite dissolution and precipitation in the presence of CO₂

changes with temperature, pressure, and pH conditions.

Reactions occur in batch systems searching for a chemical equilibrium or while fluids are flowing across the porous medium. In the latter case, the reactive transport phenomena are governed by Péclet and Damköhler numbers for small numbers of Reynolds (Fogler & Rege, 1986; Daccord et al., 1993; Golfier et al., 2002).

The Péclet number represents the relative importance of mass transport by convection and diffusion (Buijse, 1997).

$$Pe = \frac{vl}{De} \quad (7)$$

Where:

v = interstitial velocity;

l = typical length scale;

De = molecular diffusion coefficient.

The Damköhler number describes the ratio of the reaction rate to the advection rate (Buijse, 1997).

$$Da = \frac{kl}{v} \quad (8)$$

Where:

k = reaction rate;

l = typical length scale;

v = interstitial velocity

At high values of Pe and $Pe.Da$, a dominant channel (wormhole) is formed and a large increase in permeability is expected due to the dissolution process. For low values of Pe and high values $Pe.Da$, dissolution occurs mainly on the inner surface, leading to face dissolution. For very low values ($Pe.Da$), the dissolution is highly uniform. Figure 1 shows the relation between Damköhler and Péclet numbers to dissolution regimes.

2.2 Rock characterization

The rock samples used in this study were obtained from “Morro do Chaves” outcrop, “Coqueiro Seco” formation from the Sergipe-Alagoas Basin, in Brazil.

This carbonate outcrop consists of “coquina” rocks composed of bivalve lacustrine sediments, with discontinuity due to a diagenesis process. The rock presents similarities to some carbonate reservoirs within the rift section of the Brazilian pre-salt (Chinelatto, 2013; Belila, 2014). The samples have a diameter of 1.5in and 20cm length (Figure 2) and were submitted to X-Ray Micro-CT. The sample used for X-Ray Photoelectron Spectroscopy was a cube of 2cm side length.

2.2.1 X-ray photoelectron spectroscopy (XPS)

XPS is a technique for analyzing the surface chemistry of a material and can measure the elemental composition, empirical formula, chemical state, and electronic state of the

Figure 1. Wormhole formation regime vs. Damköhler and Péclet numbers (adapted from Golfier et al., 2002).

Figure 2. Sample of “Coquina” used in the experiments.

elements within a material (Thermoscientific Website, 2016). Most of the XPS studies identified the Ca (2p), C (1s) and O (1s) core-level shifts of calcium carbonate (Ni & Ratner, 2008).

The analysis was performed to understand rock composition of CaCO_3 . The XPS was carried out in a Thermo Scientific K-Alpha™+ X-ray Photoelectron Spectrometer. The aim of the paper is to study the reactions that cause dissolution and precipitation between CaCO_3 and CO_2 . Figure 3 shows the sample XPS picture. The analysis points were separated according to color. Different points were selected in the picture depending on the color presented. Three white points, three dark points, and three blue points (Matrix) were taken to analyze the surface.

A typical XPS wide scan spectrum from calcite is shown in Figure 4. All three elements comprising CaCO_3 - Ca, C, and O- were observed. Table 1 shows the atomic concentration for the nine points analyzed. Some Silicon (Si) was found and its presence is minimum compared to other main components. The presence of Aluminum (Al), Chlorine (Cl), and Sodium (Na) was found as impurity. It should be noted that XPS uses surface layer analysis and impurities are commonly found.

As seen in Figure 4, almost only Ca, C, and O were observed on the surface. Residues of Aluminum (Al), Chlorine (Cl), and Sodium (Na) were found in the sample. These impurities may come from sodium carbonate, one of the reactants for the CaCO_3 synthesis, or from the sample plugging operation.

2.2.2 X-Ray Micro-CT

X-Ray Micro-CT is a nondestructive technique that renders information, in two or three dimensions, on processes and variables of importance to subsurface flow and transport phenomena. Various studies use X-Ray Micro-CT

Figure 3. Image of the rock surface showing two out of the nine points picked for analysis.

Figure 4. XPS wide scan of calcite showing that Ca, C, and O obtained at LNNANO facilities.

Table 1. XPS atomic concentration (%).

Element	White 1	White 2	White 3	Dark 1	Dark 2	Dark 3	Matrix 1	Matrix 2	Matrix 3	Average
O 1s	30.61	32.15	29.31	22.02	23.61	33.49	30.79	30.02	31.06	29.22889
C1s	36.19	29.3	33.92	46.56	41.64	21.77	26.11	33.93	23.48	32.54444
Ca 2p	9.65	9.00	10.39	6.91	7.38	5.83	9.17	7.05	9.98	8.373333
Ca 2s	5.76	4.79	6.53	4.23	4.59	3.66	5.68	3.82	6.41	5.052222
Ca 3s	4.86	5.84	5.64	5.57	6.01	4.60	7.14	4.34	7.44	5.715556
Ca 3p	12.93	12.27	14.21	11.16	12.84	11.32	16.18	12.56	17.14	13.40111
Si 2p	-	3.98	-	1.61	1.72	7.30	2.61	4.57	1.29	2.564444
Si 2s	-	2.67	-	1.49	1.71	6.18	2.32	3.71	1.41	2.165556
Cl 2p	-	-	-	0.45	0.50	-	-	-	0.82	0.195556
Al 2p	-	-	-	-	-	2.72	-	-	-	0.302222
Al 2s	-	-	-	-	-	3.13	-	-	-	0.347778
Na 1s	-	-	-	-	-	-	-	-	0.97	0.107778

for rock characterization and for reactive transport phenomena studies (Gharbi et al., 2013; Andrew et al., 2014; Amin et al., 2014; Mattilaa et al., 2016). The X-Ray Micro-CT was carried out in a GE Phoenix V|Tome|x L300 X-Ray Micro-CT.

The image analysis consisted of the use of common image processing techniques such as

contrast handling, segmentation, erosion, and dilation. Our study used the MIPAR software (Sosa et al., 2014), developed by the Center for the Accelerated Maturation of Materials (CAMM) at Ohio State University, for the 2D analysis. Figures 5 and 6 show the pre and post-analysis of a sample slice.

Figure 5. Image slice obtained from X-Ray Micro-CT: 5a original image; 5b overlay with 30% opacity.

Figure 6. Images from X-Ray Micro-CT: 6a outline of pore walls; black and white image with pores in black; and 6c number of pixels present in each pore.

Figure 7. Porosity along the sample length.

Figure 7 shows the porosity along the sample length. The X-Ray Micro-CT data set is composed by 5,866 slices along the 20 cm sample length. The porosity was calculated at each slice. As seen on the plot, porosity varied between 6.04% and 11.79% (minimum and maximum porosities found at slices). The average porosity calculated for the entire data set was 9.23%.

Figure 8. Analyzed Volume of Interest (VOI) in the investigated sample.

Figure 9. Volumes rendering: a) solid volumes b) pore network.

A 3D image was created to show the sample reconstruction after the X-Ray Micro-CT data. Typically, the starting point of the 3D image analysis consists of the extraction of a representative Volume Of Interest (VOI), usually denoted as Representative Elementary Volume (REV) in the assumption that the porous space is represented by the sample under investigation (Brun et al., 2010). Although there are suggested rules for REV size determination (Bear, 1972), the process itself is handled on a case-by-case situation by the user. In this study, we used the iMorph software (Brun et al., 2008; Brun et al., 2009) for 3D reconstruction and analysis.

Figure 8 shows the VOI (red area) used in the analysis. The X-Ray Micro-CT generates 5,866 slices representing an analyzed volume of 1214x1199x5866 in 20cm length. The need of a powerful computer interfered in the image analysis and segmentation was necessary to continue the analysis. We used only 59 slices, representative of the analyzed volume of 269x269x59 pixels, which represented 2 mm length in the sample. It is worth reminding that such value represents the minimum distance between two slices of a conventional tomography. Figures 9a and 9b show the volume rendering of the sample and the pore network, respectively. The average porosity calculated in the VOI was 9.76%.

2.2.3 Mercury injection capillary pressure (MICP)

Mercury intrusion capillary pressure (MICP) test is a common technique to evaluate the pore-throat size distribution. In a mercury intrusion test, the non-wetting Mercury invades the connected pore system according to the imposed pressure

Figure 10. MICP test sample.

(Qajar, 2012). Figure 10 shows the sample (2 cm x 2 cm x 2cm) that was subjected to MICP. The mercury injection was carried out in a Micrometrics Autopore IV 9500 porosimeter.

First, the sample was inserted into a low-pressure chamber and submitted to vacuum. The operating range adopted in this step was 0.5 to 20 psi. After the mercury filling in a low-pressure operation, the sample was moved to the high-pressure chamber where pressure ranged from 20 to 60000 psi. At each set pressure value, the intruded mercury volume was registered. The set of measurements provided a curve of cumulative volume of mercury to successive pressure increases (Figure 11). The pore-throat diameter associated to the incremented volume is represented in Figure 12.

The measured porosity of 10.96% is consistent with those found in the literature (Chinelatto, 2013; Belila, 2014). The maximum pore-throat diameter value found was 401.5 μm and the

Figure 11. Cumulative Intrusion vs. Pressure for MICP test.

Figure 12. Incremented volume vs. Pore-Throat Diameter.

Figure 13. Histogram showing the distribution of pore-throat sizes.

Figure 14. Experimental apparatus for CO₂ saturated brine injection.

minimum 0.01 μm , but one can observe that the rock is formed, mostly, by large pores. Figure 13 shows the percent frequency interval between macropores, mesopores, and micropores (Marzouk et al., 1995; Ramamoorthy et al., 2008; Machado et al., 2011). The sample has 5.48% of micropores, 27.97% of mesopores, and 66.55% of macropores.

Although few micropores are present, the distribution is heterogeneous (large diameter variation). The results obtained by Micro-CT and MICP are shown in Table 2 with porosities ranging from 9.23% to 10.96%.

2.3 Description and application of equipment and processes

The experimental apparatus used in the displacement study is located at the University of Campinas. Figure 14 shows the experimental setup scheme. The injection system includes fluid supply cylinders, automatic high-pressure pumps, and flow meters. All equipments are specified to operate with corrosive fluids at high pressures and temperatures. The high-pressure cylinders, tubes

Table 2. Porosity values for different methods of measurement.

Method	Analysis	Mean porosity (%)
X-Ray Micro-CT Scan	2D	9.23
X-Ray Micro-CT Scan	3D	9.76
MICP	-	10.96

Table 3. Brine composition in wt. %.

NaCl	BaCl ₂	KCl	MgCl ₂	CaCl ₂	SrCl ₂	KBr	NaHCO ₃	LiCl	Na ₂ SO ₄
14.7356	0.0004	0.7300	0.3289	2.4707	0.0358	0.0476	0.0076	0.0766	0.0117

and valves, and connections are made of a highly resistant material to corrosive media and present a high mechanical strength. The system's maximum operating conditions are 10,000 *psi* and 150 °C, allowing reproducing reservoir conditions.

For the proper preparation of the rock sample, a protection system was developed for the rubber used in the core holder. The rubber usually enters the rock pores when subjected to overburden pressure. To avoid being exposed to this type of pressure, the sample is first wrapped with Teflon, then, in sequence, aluminum foil, and Teflon again. Finally, it is coated with retractable plastic materials encroached by heating. This procedure was used successfully for handling CO₂ injection.

After being inserted in the core holder, the sample was submitted to a 3,000 *psi* overburden pressure and, then, it was cleaned. The cleaning procedure comprised a sequential injection of methanol (1ml/min) at room temperature (22 °C) to remove salts from the sample, toluene (1ml/min) to remove organic components, and dry

nitrogen to help the drying process. Then, compressed air (6 bars) was injected for 48 hours to aid drainage. In sequence, rock porosity was determined by gas expansion technique using a nitrogen porosimeter Ultra-Pore 300, and the absolute permeability with an Ultra-Perm 500, both from CoreLab Instruments.

The injected fluid was brine, saturated with sc-CO₂. Brine at high concentrations (200,000 ppm) composed by a mixture of salts (NaCl, KCl, MgCl₂, CaCl₂, BaCl₂, SrCl₂, LiCl, KBr, Na₂SO₄, and NaHCO₃) was prepared to saturate the sample and compose the injected fluid. X-ray computed tomography (X-ray CT), developed for medical purposes, was used to perform sample scanning during the experiment. The brine composition used is detailed in Table 3.

3. RESULTS

The tests were performed for three injection rates of brine saturated with sc-CO₂ (0.05, 0.1, and 0.5 cc/min) at 25°C and 2,000 *psi*. The confining pressure was constant and equal to 3,000 *psi*. At each different injection rate, a total of 4 pore volumes were injected. At the completion of each pore volume, a CT scan was held to check porosity changes along the sample. Table 4 shows the sample initial properties. Table 5 shows the tested injection rates.

Figure 15 shows the evolution of the average porosity obtained by CT scan along the development of the tests with three different injection rates and with a standard deviation of 0.31. During the injection of the first 2 pore volumes the average porosity increased, and in sequence the mean porosity dropped. This may have been due to the low flow rate that, after calcite dissolution, could not remove the solids through the porous network. After the injection of 4 pore volumes, at $q = 0.1 \text{ cm}^3/\text{s}$, porosity changes were less abrupt, although the flow rate was not

Table 4. Sample properties.

Sample parameters	
mass (<i>g</i>)	505.06
length (<i>cm</i>)	20.2
volume (<i>cm</i> ³)	229.08
permeability (<i>mD</i>)	128

Table 5. Test injection rates.

Process	Injection rate (<i>cc/min</i>)
Saturation	-
Injection	0.5
Injection	0.1
Injection	0.05

Figure 15. Mean porosity obtained by CT scan.

Figure 16. Relative porosity change for five segments composed by 4 centimeters for each injection rate.

too high, in fact, it was at the order of magnitude common in natural groundwater systems. After the injection described above, the reactions appeared to be strong in the first pore volumes injected during the process. At a high flow rate ($q = 0.5 \text{ cm}^3/\text{s}$), there was a persistent increase in porosity. The occurrence was probably due to dragging of the loose grain out of the plug by the high flow rate.

To improve the visualization of the porosity changes in the sample, Figure 16 shows the relative

porosity change for five segments composed by 4 centimeters for each injection rate. There is a high porosity change in the first regions (injection well) compared to the last regions (towards the production well). As a general rule, non-uniform dissolution is expected to occur with the first pore volumes injected and near the injection well in calcite-rich reservoirs because of the high reactivity of calcite at low pH conditions. As the flow moves down the sample, the chemical potential of CO_2 brine solution is reduced and dissolution becomes less effective.

4. CONCLUSIONS

The rock characterization by XPS technique showed that the rock composition is formed practically by CaCO_3 . Peaks of Ca, C, and O were clearly dominant, with some traces of Aluminum (Al), Chlorine (Cl), and Sodium (Na) also found in the sample. These impurity traces may come from the sodium carbonate, one of the reactants for CaCO_3 synthesis, or introduced by the sample plugging operation.

The porosity characterization through X-Ray Micro-CT and through MICP show a good correlation between the values found. The 2DX-Ray Micro-CT analysis using MIPAR Software found 5,866 porosity values through the 20cm length. The mean porosity of 9.23 is close to that found in the 3D analysis (9.76%) using iMorph software. One must be cautious when analyzing 3D porosity as it depends on the REV size determination. The MICP analysis showed a porosity value of 10.96%. The techniques furnish the pore size distribution. The maximum pore diameter value found was 401.5 μm and the minimum 0.01 μm .

The results of the displacement test show the porosity changes due to supercritical CO_2 enriched brine. The three different injection rates induced different behaviors to the changes. The first injected 2 pore volumes to promote an increase in porosity, but, then, the effect stabilized for a while. When the injection rate was increased to 0.5 cc/min it seemed to expel the fine grains after the chemical dissolution re-starting the increase in the open pore volumes.

ACKNOWLEDGEMENTS

The authors would like to acknowledge the financial support provided by PETROBRAS and for the research support by LNNano - Brazilian Nanotechnology National Laboratory- and CNPEM/MCTI, for the collaboration with the XPS analysis. The authors would also like to recognize the following staff members: Wellington Fernando Marson, Washington Botine, and Erika Tomie K. Blini, of the Laboratory of Miscible Methods of Petroleum Recovery at the Center for Petroleum Studies, University of Campinas, Brazil.

NOMENCLATURE

XPS = X-ray Photoelectron Spectrometer
 CNPEM = Brazilian Center for Research in Energy and Materials
 CENPES = Petrobras Research and Development Center
 CAMM = Center for the Accelerated Maturation of Materials
 MIPAR = Materials Image Processing and Automated Reconstruction
 VOI = Volume Of Interest
 REV = Representative Elementary Volume
 MICP = Mercury intrusion capillary pressure

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