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Kinetics of carbonate dissolution and its effects on the porosity and permeability of consolidated porous media

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ABSTRACT

Injection of carbon dioxide into carbonate oil reservoirs is expected to promote chemical dissolution of the rock and alter its petrophysical properties. This work reports an experimental investigation on porosity and permeability alterations of carbonate samples due to the acid action of the carbonated water produced by means of solubilization of carbon dioxide in an aqueous solution. Travertine marble rocks with properties similar to Brazilian pre-salt reservoir rock were used in the tests at 9000 psi and 65 °C. Dissolution was carried out in high-pressure vessels during a total period of 240 h. Reaction was stopped at intermediate time intervals to evaluate porosity, permeability and mass loss of the samples. Results showed that the dissolution reaction between the travertine and carbonated water presents a slow kinetic, leading to a small loss of 0.2 g of sample after 240 h of reaction. However, the minor mass loss impacts strongly on the porosity and permeability of the rock. Data show that a variation of 1 wt.% on the sample mass caused by dissolution produces a change of 50% on the sample porosity and of 180% on the sample permeability. The dissolution rate is greatly faster if carbonated water is replaced by HCl aqueous solution and depends on the acid solution concentration. In addition, results lead to an exponential model that allows forecasting the mass loss as a function of time. Knowledge on the dissolution rate of carbonate samples by carbon dioxide solutions is required in EOR and CO_2 storage projects to estimate the changes on the flow properties of the porous formation and the damages that can be impinged to the rock.

1. Introduction

Interactions between water and rock occur during oil recovery methods that apply aqueous fluid injection into reservoir. These interactions are particularly important when carbon dioxide is used as injection fluid in carbonate reservoirs. This is relevant in CO_2 sequestration projects in deep saline aquifers, also in carbonate rock reservoirs. It is well known that when CO_2 dissolves in water, carbonic acid (H_2CO_3) is produced. The resulting acid water will react with the carbonate salt ($CaCO_3$ and $MgCO_3$) present in the rock causing its dissolution. This reaction is expected to cause changes in the main petrophysical properties of the reservoir rock, such as permeability and porosity (Luquot and Gouze, 2009).

It has been observed during carbonate dissolution experiments that the rate of calcite dissolution when contacted by an acid solution is influenced by the transport rate of reactants to the surface, the kinetics of the surface reaction, and the transport rate of products away from the surface (Fredd and Fogler, 1998). Also, differences in the acid action have been identified on the dissolution of the several types of carbonate. The dissolution rate of dolomite is slower than that of limestone for instance. Dolomite dissolution is mainly homogeneous and determined by surface reaction (Liu et al., 2005) and it tends to be directly proportional to the calcium carbonate concentration in the aqueous phase. However, this trend is not followed if substantial amounts of clay are present in the rock sample. The salt dissolved can precipitate like fine grains that might cause formation damage in tight carbonate reservoirs (Taylor et al., 2006), this effect was pointed as the responsible for reducing the permeability (Bacci et al., 2011).

Alternating injection of CO_2 and brine produced an increase of both porosity and permeability, followed by a decrease in these properties, which resulted from the following dissolution and precipitation, respectively. In these cases, permeability reduction may reach up to 50% (Grigg et al., 2005), this behavior was later confirmed by experiments evaluating the interactions between CO_2, water, oil and carbonate rock (Zekri et al., 2009).

Further tests with CO_2 as an injection fluid were done, with a deeper knowledge of the changes occurring inside the plugs by

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computerized tomography, which allowed to state the relation of the dissolution–deposition process and the volume of fluid injection, regardless of the salinity of the fluid or the rate of injection (Izgec et al., 2005). In addition, permeability showed an increase near the injection point and a decrease at farther locations, this data could be related in a $k–\phi$ function based on the reactivity of the fluid that first percolates a certain region of the rock (Luquot and Gouze, 2009).

Changes in the reactive surface area of limestone samples during a flow experiment with CO_2 showed that the dissolution occurs incisively in the highest pore connectivity locations and also that porosity had a slight decrease (Noiriel et al., 2009). SEM analyses have pointed out that calcite grains seem to be attached to very few ultrafine particles, while dolomite grains presented more adhered ultrafine particles. The decrease in the specific surface areas of dolomite is most likely due to a fast preferential dissolution of the fine particles and other highly soluble phases during the short period of the test.

The present study aims to investigate the changes in mass, porosity and permeability due to the dissolution of Italian travertine samples when they are contacted by an acid aqueous solution of CO_2 in water under high pressure and reservoir temperature conditions.

2. Experimental section

The dissolution kinetic of reactions between carbonate and acid solutions was evaluated by mass loss of the samples after the reaction time. Porosity and permeability were determined by conventional procedure, since they are the main properties involved in flow in porous media.

2.1. Materials

In the present study, carbonate rock samples were extracted from Italian travertine outcrop rocks of the kind regularly furnished for masonry work. The reason to pick such rock is the alleged similarity to formations encountered in the pre-salt reservoirs. Travertine samples were plugged as cylinders with 1 in. diameter and 0.65 in. height. Carbon dioxide was obtained from Air Liquide (99.999%), NaCl was obtained from Chemco (> 99.0%) and water was mili-Q quality.

Fig. 1 presents the X-ray diffractogram obtained while evaluating the chemical composition of the rock samples used in the study. Analysis shows that the travertine is composed of 86.53% of carbonaceous mineral in the form of calcite and 13.47% of quartz in several crystallographic phases.

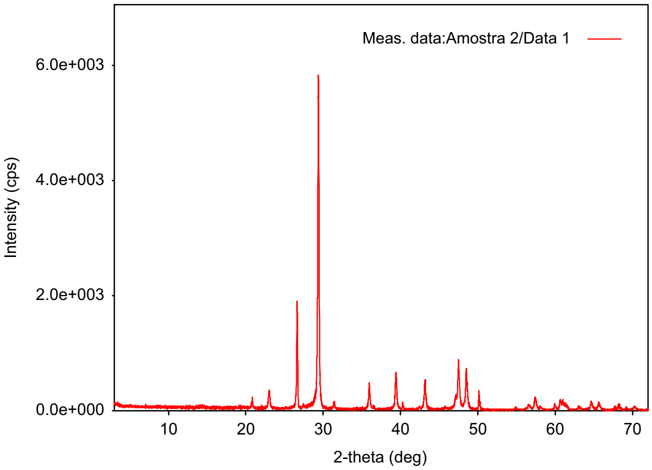

Fig. 1. X-ray diffraction of travertine rock samples: 86.53% calcite and 13.47% quartz.

2.2. Methods

2.2.1. Sample preparation

The rock samples were first cleaned in a two-step soxhlet extraction procedure using ethanol and toluene, respectively, to remove inorganic and organic residues. After cleaning, the samples were dried at 80 °C during 16 h. At this initial condition measurements of mass, porosity and permeability were registered for each sample. At the next step, the samples were inserted in a closed high-pressure vessel and saturated with 20 mL of a 35,000 ppm NaCl aqueous solution under vacuum during 12 h. The mass of each of the vessel–sample–brine ensemble was registered.

2.2.2. Dissolution test

Dissolution of the travertine was evaluated through the mass changes promoted by the reaction between the rock sample and the carbonate water (CO_2 in water solution) in which the rock was immersed. Dissolution tests were carried out in closed high-pressure vessels (HPV) through five successive reaction cycles totaling 240 h apiece. After each reaction cycle, the mass, porosity and permeability of each rock sample were measured.

The procedure consisted of the injection of pure CO_2 into the HPV cell, containing the saturated sample, such as described early. The HPV cell ensemble containing the rock sample, brine and carbon dioxide was left in an air heater bath at the constant at temperature of 64 °C during the time span of the test. This temperature was chosen for being the typical temperature for Brazilian Pre-salt reservoirs. CO_2 was injected into HPV by means of a high pressure displacement pump (DBR, USA) up to the assigned pressure (4500 and 9000 psi). Then, the vessel was kept at rest for the given reaction periods, which were composed of a sequence of the following periods, each one representing a reaction interval: 24 h, 24 h, 48 h, 72 h and 72 h. After completion of every reaction interval, samples were removed from the HPV cell and inserted into a hot water bath in order to remove fine grains of precipitated salt from both inside the porous space and the external surface of the sample. To assure the total removal of precipitated salt from the samples, the salinity of the water bath was monitored by a conductivimeter. Whenever the water conductivity reach a constant value, the water containing the removed salt was replaced by de-ionized water, until any conductivity could be detected. Finally, samples were again dried and the aforementioned properties re-determined. At this situation, the cleaned and dried samples were again saturated and placed in the HPV cell at the same preceding pressure, to follow with the next reaction time step.

Fig. 2 illustrates the scheme of the experimental apparatus. The setup is configured by a positive displacement pump connected to a high pressure cylinder containing carbon dioxide. The pump displaces a hydraulic oil that is injected into a high pressure cylinder to move a piston to finally displace CO_2 into the HPV cell. The injection pressure is monitored by both a pressure differential transducer located at the pump and a precision manometer installed at the reactor. Table 1 shows the CO_2 in brine concentration used in the dissolution tests for each travertine sample.

2.2.3. Porosity measurements

Porosity was determined by an Ultra-pore 300 Helium System (CoreLab Instruments, USA). The Ultra-Pore 300 uses two interconnected compartments and data from reference standards to measure the grain and pore volume of the rock and then to calculate the porosity.