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Study of carbonation in a class G Portland cement matrix at supercritical and saturated environments

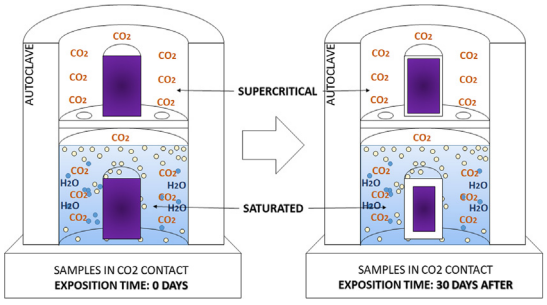
Bruno Leonardo de Sena Costa *, Julio Cezar de Oliveira Freitas, Paulo Henrique Silva Santos, Romero Gomes da Silva Araújo, Juan Fábio dos Santos Oliveira, Dulce Maria de Araújo Melo

Laboratório de Cimentos, Federal University of Rio Grande do Norte, Natal, Rio Grande do Norte 59072-970, Brazil

HIGHLIGHTS

- CO_2 in a same pressure vessel in supercritical condition and dissolved in water.
- Effects of supercritical CO_2 and saturated CO_2 in water in the cement matrix.
- Investigation of carbonation caused by the medium with supercritical CO_2.
- Investigation of carbonation caused by CO_2 dissolved in water.
- Comparative analysis of samples of carbonated cement.

GRAPHICAL ABSTRACT



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ABSTRACT

The carbon dioxide (CO_2) is a chemical compound that can be present at subsurface, inside the porous of reservoir rocks containing oil or natural gas, dissolved or free. Being its occurrence natural or artificial, when injected into the reservoir at high pressure in order to improve the oil recovery factor. Regardless the source, it has potential to cause serious problems to the cement used during certain operations in oil wells. When in contact with hydration products of the Portland cement, the CO_2 reacts due to a specific phenomenon denominated carbonation. This transformation significantly affects the cementitious composite array, causing changes in the microstructure, chemical compounds and harmful consequences for physical properties, such as porosity/permeability and mechanical resistance. The present study investigated the effects of CO_2 under two conditions, supercritical state and dissolved in water, in a class G Portland cement matrix that is used in the oil industry. Samples containing the same formulation were placed at the same time in an autoclave, exposed to mediums with supercritical CO_2 or saturated in water and removed after 30 days. In order to corroborate in the discussions and conclusions, the following analyses were conducted: pH indicator for measuring carbonation depth, image analysis to quantify the percentage of the affected area, X-ray diffraction using the Rietveld method for phases identification and quantification, and thermogravimetric analysis in order to confirm the presence of certain compounds. The analysis showed very distinct results, being the samples that were exposed to saturated medium suffering a greater attack. Based on the images analysis, formation of carbonates identified by XRD and quantified by the Rietveld method, the attack on samples subject to the medium saturated with CO_2 was 35 percentage points higher when compared with the supercritical medium.

* Corresponding author.
E-mail address: bruno_engmat@yahoo.com.br (B.L. de Sena Costa).

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1. Introduction

The primary oil well cementing is one of the most important steps in the construction process of an oil well. They are operations performed at the end of each phase drilled, being aimed to cement a column composed by casing pipes that are connected and located at a certain depth. After the hardening process, the cement provides mechanical stability, protects the casing from corrosive fluids generated by the rock formation, being also responsible to avoid communication between zones of permeable rocks containing various fluids [1].

Operations involving the use of Portland cement are also used in others activities during the productive life of the well. These operations aim to correct failures in primary cementing, holes in the casing, insulation of adjacent rocks, etc. At the end of its productive life, the wells are sealed with cement plugs, resulting in a total isolation between the subsurface and surface [2].

The formulation of a cement slurry consists, basically, in the mixture of cement, water and solid and/or liquid chemical additives. These additives are used to adjust the fresh slurry properties and promote desirable characteristics after hardening [1,3]. The cement used by the oil industry is produced under rigorous international standards to ensure specific physical and chemical properties. Such requirements are intended to ascertain support during many years the harsh pressure and temperature environments exposed in this paper [1,4].

The cement is a hydraulic material, the contact of its particles with water results in exothermal reactions that lead to the formation of new products. The most common compounds of the anhydrous cement are: tricalcium aluminate (C_3A), tetracalcium aluminoferrite (C_4AF), tricalcium silicate (C_3S) and dicalcium silicate (C_2S). Cement hydration reactions have been widely investigated and discussed by several authors [4–8], forming products according to the reactions shown below.

Hydration of the calcium silicate mineral (C_3S and C_2S):

$$C_3S + (1.3 + x)H \rightarrow C_{1.7}SHx + 1.3CH \quad (1)$$

$$C_2S + (0.3 + x)H \rightarrow C_{1.7}SHx + 0.3CH \quad (2)$$

Where: H is water; $C_{1.7}SHx$ is calcium silicate hydrate; CH is calcium hydroxide.

Hydration of the calcium aluminate/ferrite minerals (C_3A and C_4AF):

$$2C_3A + 21H \rightarrow C_4AH_{19} + C_2AH_8 \rightarrow 2C_3AH_6 + 9H \quad (3)$$

$$C_3A + 3C\underline{S}H_2 + 26H \rightarrow C_6A\underline{S}_3H_{32} \quad (4)$$

$$2C_3A + C_6A\underline{S}_3H_{32} + 4H \rightarrow 3C_4A\underline{S}H_{12} \quad (5)$$

$$C_4AF + 3C\underline{S}H_2 + 21H \rightarrow C_6(A,F)\underline{S}_3H_{32} + (F,A)H_3 \quad (6)$$

$$C_4AF + C_6(A,F)\underline{S}_3H_{32} + 7H \rightarrow 3C_4(A,F)\underline{S}H_{12} + (F,A)H_3 \quad (7)$$

Where: C_3AH_6 is hydrogarnet; $C\underline{S}H_2$ is gypsum; $C_6A\underline{S}_3H_{32}$ is ettringite (AFt); $C_4(A,F)\underline{S}H_{12}$ is monosulfoaluminate (AFm); (F,A)H_3 is an amorphous phase that were forms in small amounts.

The reactions described previously start to occur from the first contact of the water with the cement particles, these reactions are non-linear with time, they are intense at first, led by aluminates and by C_3S, and tend to decrease, because of array densification and C_2S slow reaction [4,7].

One of the major problems that can occur when the matrix has hydration products formed and/or in formation happen when this material is exposed to a corrosive medium consisting of carbon dioxide (CO_2) [9–11]. This is a challenging situation for the project team responsible for the oil wells cementing.

The contact between cement and CO_2 can happen in different forms: either when it is already naturally present in rock pores, or when it is injected at high pressure in the well in order to improve the oil recovery or for geological storage.

1.1. Carbon dioxide characteristics

Similar to other segments of the production chain, the oil and gas industry also has advanced in technologies that aim to treat and provide an appropriate destination to CO_2. When this compound is dissolved in hydrocarbons (HC), the gas is separated at the surface and injected back into the reservoir, in order to increase the productivity index [12–14] and, consequently, the wells production. Unfortunately, in cases in which a series of factors, such as lack of technology, technical and economic infeasibility, impossibility of reinjection due to geological characteristics, thermodynamic limitation, etc., it is impossible to implement reinjection systems, making the CO_2 an important environmental passive.

In natural or confined controlled processes, the carbon dioxide can present itself in different states, depending on the environment conditions. In a controlled environment, such as a pressure vessel, when in the presence of water and subjected to specific pressure and temperature conditions, the gas may present itself as a supercritical fluid and, also, solubilized into water.

The term "supercritical" is associate to the state when the fluid is taken above a threshold value of pressure and temperature. The exact combination of these two variables is denominated "critical point", resulting in specific properties for each substance. When in supercritical state, the fluid is not in a solid, liquid and neither a gaseous state. In Fig. 1, it is possible to observe the compound behavior in a phase diagram. At standard temperature and pressure, the CO_2 is in the gaseous state, at low temperatures it is solid, so the physical state of CO_2 varies depending on the conditions in which it is submitted [15].

When it reaches the supercritical state, 31.1 °C and 7.29 MPa, the CO_2 cannot be liquefied, regardless the pressure. In this state, it is not possible to distinguish between liquid or gas, so the supercritical fluid behaves as a gas in terms of compressibility and viscosity, and has a density similar to a liquid. It should be noticed that when contained in the rocks pore of the reservoir the CO_2 physical state depends on the depth, according to the conditions presented in the diagram from Fig. 1. Studies state [16,17] that in a large number reservoirs the carbon dioxide remain in the supercritical form.

Carbon dioxide is a water-soluble compound [18]. The contact with the aqueous medium partially dissolves the CO_2 in the water, however, despite the miscibility, there are considerations such as partial pressure, solubility and salinity that can limit the dissolution of gas in liquid.

Carbon dioxide dissociation:

$$CO_2 + H_2O \leftrightarrow H_2CO_3 \leftrightarrow H^+ + HCO_3^- \leftrightarrow 2H^+ + CO_3^{2-} \quad (8)$$

The solubility of gases in liquids is described by Henry's law, which states that: *"in ideal dilute solutions and at a constant temperature, the solubility of a gas in a liquid is proportional to the partial pressure of the gas in contact with this liquid"* [19]. This concept explains the fact that CO_2 dissolved in water is susceptible to variations when exposed to different conditions of temperature and pressure. When there is a pressure increase, the carbon dioxide tends to increase its water solubilization degree, that is, the higher the pressure exerted on the liquid substance, the higher the collisions force of molecules with the medium and more molecules will be able to penetrate and dissolve reaching a CO_2 saturated