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Carbonation in oil well Portland cement: Influence of hydration time prior to contact with CO_2

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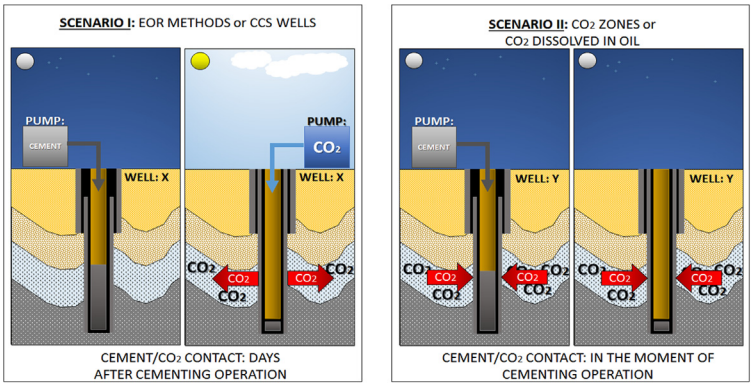
HIGHLIGHTS

- Different scenarios: CO_2 naturally present in rock or artificially injected.
- Exposure to CO_2 and analysis of influence on the cement hydrated previously.
- Analysis of the progress of carbonation and characterization of the formed phases.

GRAPHICAL ABSTRACT



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ABSTRACT

When Portland cement slurries comes in contact with carbon dioxide at the subsurface, can suffer serious problems by carbonation. The contact between the hydrated cement products and CO_2 occurs when it is injected into the well, after the primary cementing or when it is already present in the rock formation. In all situation, the cementing design should consider the best conceptual and operational practices, in order to ensure a greater integrity during the entire life of the well. In this work, three slurries with the same formulation were investigated. Samples were cured during 8 h, 7 days and 28 days before contact with carbon dioxide. Different curing times are aimed to simulate earlier time and later time contact between cement and CO_2. In autoclave, samples were submitted during 30 days in water saturated with CO_2. Before autoclave, the samples were analyzed by XRD. After the carbonation, mass, and density were measured, the carbonated area was calculated and XRD was run again. The results showed different processes, but similar carbonation results at the end. The sample after 7 days of curing showed more carbonation than samples after 8 h and 28 days. In other hand they showed different preservations mechanism.

1. Introduction

Every year several new oil wells are drilled around the world. Even so, there are still a huge number of old wells in full production, declining it, or in an abandonment process. In the well construction, there is a very important step called primary

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cementing. During this operation, one or more cement slurries are placed in the annular space, between the metallic casing and the rock formation, in order to protect the casing from corrosive formation fluids, to promote mechanical stability for the well and to isolate permeable zones preventing undesirable communication between them [1]. Throughout its life the well can withstand the environmental and operational requirements and the cementing step must be carried out effectively [1,2]. If the best conceptual and operational practices are not planned earlier and/or are not embraced during the cementing job, there are a big chance to face serious problems with the well. These problems can many times be solved throughout expensive corrective operations. However, sometimes, is the best decision may be the well abandonment.

In petroleum industry a specific scenario which demands special attention is the construction of a well in carbon dioxide (CO_2) environment [3,4]. Injection of carbon dioxide can be used at the petroleum industry as a technic for enhancing oil recovery or could be present in the porous media of rock reservoir. The CO_2 in contact with the cement array reacts with hydrated Portland cement. The reaction products are calcium carbonate, calcium bicarbonate and silica gel [4]. This phenomenon is called carbonation and it is a undesirable and critical situation for the well. The advance in the reaction process leads to bi-carbonation and Ca-leaching, which are quite damaging to cement. After been affected by this phenomenon, the cement matrix decays, its physical and mechanical properties become seriously compromised, where the loads that act on the cement sheath increase the formation of microcracks and there is a great chance of material failure. Several researchers have reported studies showing deleterious effects of CO_2 in Portland cement slurries [4–7]. The chemical reactions that occur between the hydrated cement products and the CO_2 rich medium are described below. In aqueous medium the carbon dioxide undergoes dissociation:

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

The carbonic acid formed in (I) continues to react with the cement hydration products (II–V), transforming $Ca(OH)_2$ (calcium hydroxide) and C—S—H (calcium silicate hydrate) into $CaCO_3$ (calcium carbonate).

$$Ca(OH)_2(s) + 2H^+ + CO_3^{2-} \rightarrow CaCO_3(s) + 2H_2O \quad \text{(II)}$$

$$C—S—H(s) + 2H^+ + CO_3^{2-} \rightarrow CaCO_3(s) + SiO_xOH_x \quad \text{(III)}$$

$$Ca(OH)_2(s) + H^+ + HCO_3^- \rightarrow CaCO_3(s) + 2H_2O \quad \text{(IV)}$$

$$C—S—H(s) + H^+ + HCO_3^- \rightarrow CaCO_3(s) + SiO_xOH_x(s) \quad \text{(V)}$$

The carbon dioxide can meet the cement matrix in different chronological stage. In each stage CO_2 will find different hydrated products hence the chronological factor becomes a considerable variable. It means that time and the chemical nature of cement are relevant to the carbonation reactions. Products formed from hydration reactions of the Portland cement, C_3S, C_2S, C_3A and C_4AF, can be found in the extensive literature regarding this theme [1,8–12]. Based on the basic chemical reactions concepts of the Portland cement, it is possible understand that in a short period of time a few cement hydration compounds are formed, and after a long period, a greater amount of this products are formed.

Three distinct curing time intervals were ran in this study. A curing time of 8 h was established to investigate the situations where the CO_2 would already be present in the porous media of the rock formation; an intermediate curing time of 7 days was established to simulate the condition of injection of CO_2 into the well; and one more longer period of 28 days of cure was also stablished taking in count the same scenario of CO_2 injection. Studies point that around 28 days of curing Portland cement hydration reactions reach approximately 70% of reaction products stabilizes [8] and the following reactions are much slower, if no more reagents were added to the medium. The interval of 8 h was arbitrarily adopted, once that at this time the sample is solid, enabling the execution of laboratory analyses, standardizing the steps between them. The period of 7 days was considered a short and intermediate period; however, it is enough to form a large part of the hydrated cement compounds [8].

These time intervals were assumed in order to simulate two important scenarios in well time life (Fig. 1). Scenario I shows a schematic operations of Enhanced Oil Recovery (EOR) by CO_2 injection and a well for geological storage of CO_2 (Carbon, Capture and Storage - CCS) [13–17]. Both situation was covered by the samples at 7 and 28 days of curing time. The scenario II represents situation where CO_2 would already be present in the porous media of reservoir rock, as a gas contaminant or dissolved in petroleum [5,18–21]. Sample at 8 h of curing was used to represent carbonation in

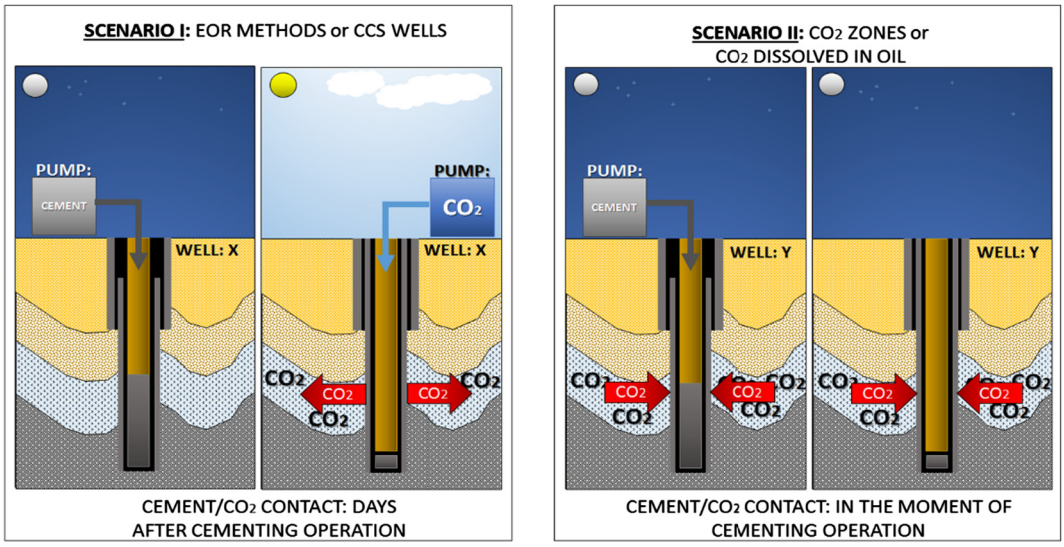

Fig. 1. Contact forms of the CO_2 with the Portland cement in an oil well.