Effects of carbon dioxide in Portland cement: A relation between static sedimentation and carbonation

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HIGHLIGHTS

- The carbonation process related with static sedimentation in class G Portland cement slurries.
- Concepts of fluid mechanics applied in the physical interpretation to cement carbonation process.
- A model for relating static sedimentation mechanism and carbonation is proposed.

GRAPHICAL ABSTRACT
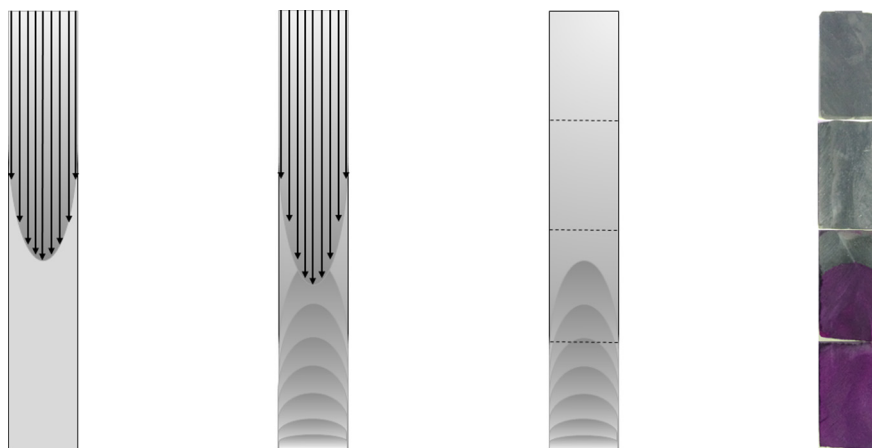
ARTICLE INFO

ABSTRACT

Two Portland cement slurries were intentionally formulated with characteristic and distinct behaviors. The slurries have in their composition conventional chemical additives that are frequently used in the cementing of oil wells and class G cement. One of the slurries have the capacity to keep the elements in suspension, producing a stable system (ST), while the other one produce particle's sedimentation, promoting an unstable system (UN). Both slurries were carbonated for 30 days in an autoclave with a CO_2 saturate environment. The carbonated samples were characterized by static sedimentation test, acid-base indicator analysis and X-ray diffraction with Rietveld refinement. It was observed that the carbonation phenomenon occurs peculiarly when the cement slurry presents sedimentation of particles. So, a model for the sedimentation and carbonation behavior was proposed for the unstable slurry based on fluid mechanics. The study proposes that stability to sedimentation is a prerequisite considered with great discretion for the studies that aim to evaluate systems submitted to the attack of CO_2. Failure to observe this prerequisite may result in inconsistent information that may lead to false positive or false negative results.

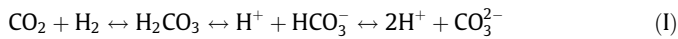© 2017 Elsevier Ltd. All rights reserved.

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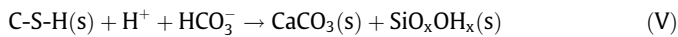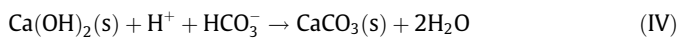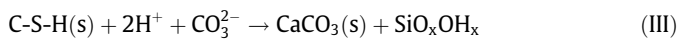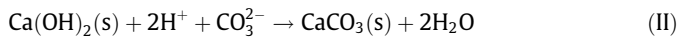
1. Introduction

Significant challenges are established at subsurface when the Portland cement hydration products are exposed to an environment that is rich in CO_2. The carbon dioxide at these environments participates in chemical reactions where, under favorable conditions, it reacts with the hydrated products of the cement, resulting in a progressive degradation and implicate on the integrity of the cement matrix, a phenomenon known as carbonation. Duguid et al. [1] describes the reactions involved in the carbonation process as follows:

CO_2 dissociation

$$CO_2 + H_2 \leftrightarrow H_2CO_3 \leftrightarrow H^+ + HCO_3^- \leftrightarrow 2H^+ + CO_3^{2-} \qquad (I)$$

Cement carbonation

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

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

$$Ca(OH)_2(s) + H^+ + HCO_3^- \rightarrow CaCO_3(s) + 2H_2O \qquad (IV)$$

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

According to the study of Lagerblad [2], a series of chemical reactions occur during the carbonation process. Lagerblad [2] says "Basically $Ca(OH)_2$ in contact with CO_2 forms $CaCO_3$ (reaction II). Water is not consumed but is needed in the transformation (reaction I). When the $Ca(OH)_2$ is consumed the pH of the cement slurry/pore solution will drop and all other hydrate phases will successively break down (reactions III–V)".

In wells that were drilled for the exploration and production of oil where CO_2 is already present in the rock formation, in oil wells that use EOR (Enhanced Oil Recovery) injection or in CCS (Carbon Capture & Storage) wells, the presence of CO_2 establishes challenges for the cementing and for the useful life of these wells. If the cementing project does not contemplate a system to combat CO_2, the cement matrix may deteriorate, jeopardizing the physical stability of the well, entailing serious risks to the environment and to the people.

The stability of a cement slurry system is fundamental in order to ensure a good hydraulic seal in the well. In a study developed by Peng et al. [3] he states "The stability of cement slurry is governed by mechanisms acting on several scales involving the movement of particles and fluid". Peng et al. [4] describes in another study that the instability phenomena in cement slurry occurs due to density differences between the basic constituents, ranging from water, 1000 kg/m³, to the solids with density of 2700 and 3150 kg/m³. According to Ganguli [5], some slurry systems are not capable to keep cement particles evenly distributed, making the heavier particles decay quickly to the bottom. Thus, after hydration, the cement matrix will have different physical properties along its structure.

In this paper, two class G cement slurries were formulated, one stable and one unstable. The objective was to evaluate the effect of carbonation on cement slurries with low stability. It was observed that the failure to not consider the stability of the slurry previously may lead to misunderstandings later on interpretation of the datas,

resulting in information considered false positive or false negative. It is possible to propose a model of static sedimentation of particles and criticality relate it with a slurry system that is obligatorily stable.

2. Materials and methods

2.1. Materials

The cement slurries were prepared by setting the density to 1.89 g/cm³ (15.8 ppg). The preparation was conducted according to API RP 10B-2 [6]. The Portland cement used was class G with a specific gravity (SG) of 3.15 g/cm³ and attends the requirements established by API Spec 10A [7]. For the preparation of the mixing water, deionized water and additives common to the well cementing industry were used. The additives used were: strength retrogression agent based on silica with SG of 2.07; Silicone defoamer with SG of 0.98; Fluid loss additive of cellulose derivative type with SG of 1.36 e; Dispersant of polycarboxylate type with SG of 1.17.

2.2. Sample preparation

Two cement slurries were prepared: the slurry with stable behavior was denominated ST and the unstable slurry UN. The concentrations of the components used for slurries formulations are presented in Table 1.

After preparation, the slurries were conditioned at 40 °C and subsequently poured into metal molds 203 mm long and a 25 mm internal diameter, according to API RP 10B-2 [6]. The metal molds with the slurries were placed in a thermostatic bath where they remained for 24 h at 70 °C and atmospheric pressure. After curing the cylindrical samples ST and UN slurries were demolded and divided into four equal parts with sizes of approximately 50 mm each. The four divisions received denominations following the order of how they were vertically cured in the thermostatic bath being named, the upper section 'Top' (T), the first intermediate section 'Intermediate 1' (I1), the second intermediate section 'Intermediate 2' (I2) and the bottom section 'Bottom' (B), as shown in Fig. 1.

2.3. Sedimentation test

Following the procedure API RP 10B-2 [6], the density variation throughout the sample was evaluated. Once cured, demolded and divided into four parts, each part had the density evaluated using the Archimedes Principle, as it is recommended by the procedure [6]. The density measurements of all sections of the samples were conducted before and after the exposure to CO_2 in the autoclave.

2.4. Carbonation experiment

The samples were submerged in water saturated with CO_2 for 30 days. The autoclave, manufactured by the company Top Industrie, has a parameter control system and the test conditions were 70 °C and 2000 psi, maintained throughout the whole period. Each section of cylindrical body was identified and placed in the autoclave in the vertical position, according to Fig. 2.

2.5. Carbonation depth

After 30 days in the autoclave all sections were removed, their densities were checked by sedimentation test and then they were sectioned in half in the longitudinal direction. The longitudinal cut generates two equal parts, exposing the central portion of the sample. The cut surfaces were cleaned and sprayed with a pH indicator. The indicator used was a solution composed by ethanol and phenolphthalein diluted in deionized water. When the indicator come into contact with the non-carbonated region it turns to the purple color what shows the high alkalinity, while for the carbonated area nothing happens.

2.6. X-ray diffraction (XRD) and Rietveld analysis

X-ray analyzes were performed using the equipment Eco D8 ADVANCE from Bruker with CuKα radiation X-ray tube. The scanning was ran in a range of 5°–80° with an increment of 0.02°, a step time of 0.2 s and with a sample port rotation of 15 rpm. The software used for identification was EVA and for quantification it was TOPAS, both from Bruker. The refinement by the Rietveld method was used to

Table 1
Compositions of the slurries ST and UN.

Sample	Components concentrations (% or gps)					
	Water (%)	Cement class G (%)	Strength retrogression agent (%)	Dispersant (gps)	Fluid loss additive (%)	Defoamer (gps)
ST	46.4	53.1	40	0.17	0.40	0.02
UN	45.8	54.6	40	0.17	–	0.02