SELF-HEALING OF CEMENT SLURRY FOR OIL WELLS CONTAINING CRystalline ADMIXTURE: EARLY RESULTS

Aline de Souza Oliveira (1), Romildo Dias Toledo Filho (1), Eduardo de Moraes Rego Fairbairn (1), Otávio da Fonseca Martins Gomes (2)(3)

(1) COPPE – The Graduate Institute of the Federal University of Rio de Janeiro, Brazil
(2) CETEM, Centre of Mineral Technology, Brazil
(3) National Museum, Federal University of Rio de Janeiro, Brazil

Abstract
In this paper we present the early results of the self-healing analysis of an oil well cement slurry containing 1% by weight of cement of crystalline admixture. The specimens cured in a bath at 60°C were pre-cracked at 7 days by splitting test until crack width of 200 μm. The healing process lasted 66 days in a 60°C water bath to reproduce pre-salt temperature conditions. The effectiveness of the healing process was verified by the mechanical recovery of the specimens after reloading. The analysis indicated that self-healing can be useful to improve the performance of the cement sheaths in oil wells.

Keywords: self-healing; recovery of mechanical properties; crystalline admixture; cement slurry; oil well.

1. Introduction

During the drilling of an oil well, primary cementing is the process of placing cement slurry in the annulus between the steel casing and the geological formation. After hardening, this hollow cylinder is called cement-sheath [1]. In Brazil, pre-salt oil and gas reserves have been discovered in 2006. In order to explore these reservoirs in ultra-deep water, many scientific and technological challenges had to be overcome. Total depth of the well can reach 7,000 meters. Layers are formed by water, followed by rocks and salt. The upper limit of pressure can reach around 90 MPa, while temperature range varies between 60-70°C [2], [3]. These extreme service conditions may result in crushing or cracking that may cause the lack of zonal isolation. This can lead to contamination of the crude oil or even catastrophic accidents if gas
could escape from the well [4]. Therefore, considering the various factors that tend to damage the cement sheath, it would be worthy if the cement slurry had self-healing properties.

In view of the high environmental aggressiveness and loading conditions of the pre-salt, the crystalline admixture (CA) used in this research corresponded to those classified as PRAH (Permeability-reducing admixtures for concrete exposed to hydrostatic conditions) as described by the ACI [5].

According to Sisomphon et al. [6] the main healing mechanism on the external surface of the crack is the precipitation of calcium carbonate, since the presence of CA boosts the dissolution of ions (Ca\(^{2+}\)) and increases the environmental alkalinity. Thus, the region close to the crack would have the optimal concentrations of the ions: (i) Ca\(^{2+}\) (released from the matrix); (ii) carbonate (CO\(_3^{2-}\)); (iii) bicarbonate (HCO\(_3^-\)). Kishi et al. [7] explain that the calcium carbonate is the product of the reaction between bicarbonate ions (HCO\(_3^-\)) or carbonates ions (CO\(_3^{2-}\)) solubilized in water, originating from the crystalline additives, and Ca\(^{2+}\) ions from the concrete.

From the perspective of internal healing, which results in increased mechanical properties, Sisomphon et al. [8] found that the predominant mechanisms are further hydration and the expansion of anhydrous grains. In view of this, the hydrates produced in greater quantity were CaCO\(_3\), C-S-H and ettringite. Jiang et al. [9] classified the action of CA into three types: (i) crystallization-precipitation, in which the admixture can supply CO\(_3^{2-}\) (carbonate ions) and accelerate the reaction with Ca\(^{2+}\) originated from the cement system, forming CaCO\(_3\); (ii) expansive formation associated with the presence of new hydrates with higher volume, such as AFt due to hydration of the calcium sulfo-aluminate; (iii) pozzolanic reaction with the formation of C-S-H.

No reference can be found in the use of crystalline admixture as healing agent for oil well cement slurries. Ferrara et al., [10] investigated the interaction between crystalline admixtures and disperse fiber reinforcement. They found that the material could have a better mechanical behavior after the self-healing process. De Nardi et al., [11] realized that the presence of crystalline admixtures in lime mortars enhanced self-healing. They also found that the phenomenon is more evident for specimens exposed to open air. Roig-Flores et al., [12], [13] used a high content of crystalline admixture in concretes, which reached different healing performances according to the exposure conditions. Sisomphon et al., [8] reported how the mechanical recovery of mortars is related to the chemical properties of healing products. Ferrara et al., [14] conclude that crystalline admixture accelerated the healing process and the recovery of mechanical properties. However, in accelerated exposure conditions, under high relative humidity and cycling temperature, the high dispersion of the results did not allow to draw any definitive conclusion. Jiang et al., [15] reported that crystalline admixtures combined with chemical expansive agents can accelerate the healing process.

In this paper we investigated the use of crystalline admixture as healing agent in cement slurries for oil well applications. The effectiveness of the healing process was verified by the response of the specimens after reloading. The analysis indicated that self-healing can be useful to improve the performance of the cement sheaths in oil wells.
2. Experimental program and methodology

2.1 Materials and mixture proportions of cement slurries
Cement slurry was produced with crystalline admixture, in powder form, with content of 0% and 1% by weight of cement. The water/cement ratio was fixed in 0.44. The cement used was high sulfate-resistant (HSR) class G well cement, with defoamer admixture at a dosage of 0.25% by weight of cement. Discontinuous polypropylene microfibers were added to the mixtures with 0.4% in fiber volume fraction (Vf). This low fiber content was added to guarantee cohesion between the two sides of the samples after crack opening. Proportions are shown in Table, where DE stands for defoamer admixture, PP stands for polypropylene microfibers, and CA stands for crystalline admixture. The former is commercially known as Sika WT-200P and its purpose is to seal cracks up to 400 µm and to reduce water penetration under hydrostatic pressure.

Table 1: Mixture proportions with 0.44 of w/c ratio.

<table>
<thead>
<tr>
<th>Mix code</th>
<th>Cement (kg/m³)</th>
<th>Water (kg/m³)</th>
<th>DE (kg/m³)</th>
<th>PP (kg/m³)</th>
<th>CA (kg/m³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0%CA</td>
<td>1330</td>
<td>585</td>
<td>3.3</td>
<td>4.0</td>
<td>0.0</td>
</tr>
<tr>
<td>1%CA</td>
<td>1307</td>
<td>575</td>
<td>3.3</td>
<td>3.9</td>
<td>13.1</td>
</tr>
</tbody>
</table>

2.2 Sample preparation
The mixing procedure was carried out in accordance to API-S-10A standard. The mixture passed the stability requirement of API-10B-2 standard. The slurry was poured in cylindrical moulds (Ø50 x 100 mm) that had notches positioned in two opposite diametrical positions as showed in Figure 1. They were cured in water immersion at 60°C up to 7 days in such a way that the hydration is almost complete as reported by [16] for a similar slurry. The specimens were then cut on the top, middle and bottom resulting in 3 discs (Ø50 x 25 mm), here called samples.

2.3 Pre-cracking by feedback-controlled splitting test
Pre-cracking corresponding to a single and localized crack was induced by a splitting tensile test based on ASTM C496M. The test is controlled in a twofold manner: (i) loading is controlled by the stroke displacement; (ii) a clip gage placed closed to the crack controls the end of the test for a given crack width (w). The test was carried out in a Shimadzu press with load cell of 100 kN, in constant rate of 0.5 µm/s. The preloading was automatically stopped until the crack width reached the imposed value of 200 µm.

2.4 Exposure and evaluation of healing properties
After pre-cracking, the samples were left in continuous immersion in water at a temperature of 60°C for 66 days. For this early study, we decided to submit the samples only to the typical temperature of the pre-salt wells in order to separate the various effects of this application such as pressure and salt content. After the healing period, the samples were again submitted to the splitting tensile test. The clip gage was zeroed and the end of the test was set to $w = 200 \mu m$. 
The following parameters were defined for the load-crack width curves, as displayed in Figure 2: the load at first crack \( (P_{fc}) \); the load at a crack width of 200 \( \mu \)m \( (P_{200}) \); the residual crack width \( (w_r) \); the load corresponding to the crack width of \( w_r + 200 \mu \)m \( (P'_{200}) \). The self-healing capacity was computed by means of the Index of Load Recovery \( (ILR) \) as defined in reference [14] and presented in (1). \( ILR=1 \) corresponds to total healing and \( ILR=0 \) indicates that there was no healing. Besides these values, \( ILR<1 \) would indicate that the exposure could have further damaged the cracked region, while \( ILR>1 \) corresponds to an increase of the tensile strength of the healed crack.

\[
ILR = \frac{P'_{200} - P_{200}}{P_{fc} - P_{200}}
\]  

(1)

3. Results and discussion

The samples obtained from the top of the specimens were rejected because they presented discrepant \( P - w \) curves, with values of load much lower than the samples obtained from the medium and the bottom of the specimens. Considering that the specimens passed the stability test, a first interpretation of this phenomenon indicates that there was segregation of the PP fibers. Further investigation of the positioning and fiber content will be performed to confirm this hypothesis.

Figure 3 and Figure 4 present the \( P - w \) individual curves (with lower and upper limits) and average curves for both mixtures with 0% and 1%CA contents, respectively. For the pre-cracking branch of the curve, an initial softening region can be observed after the elastic range. It is followed by a sawtooth portion indicating that the fibers are bridging the two faces of the crack. For reloading, it appeared that the samples became much more compliant after healing. Since the clip gage measures the relative displacement in a very tight region close to the crack mouths, this seems to indicate that the healed crack has elastic properties quite different from the initial ones.

The samples with 0%CA had \( ILR \) equal to 0.8, it means that the mechanical strength was not completely recovered. In contrast, the mixtures with 1%CA had average \( ILR \) equal to 1.1, which corresponds to complete healing with a slight increase in strength.

To illustrate the evolution of the healing process, we show in Figure 5 a panoramic view of a crack before and after healing assembled from micrographs obtained by a stereo microscope.
4. Concluding remarks

The early results for self-healing of the cement slurry for oil well with 1% CA studied in this paper, indicated better mechanical recovery than mixtures with 0% CA. It should be noted that the hydration of the samples was almost completed when they have been submitted to pre-cracking and exposure. Therefore, the healing process was not facilitated by the presence of unreacted anhydrous grains and it can be considered that the conditions for the onset of healing were not the most favorable.

We can then consider that these early results are very promising and that self-healing of oil well cement sheaths may become an important research topic in the coming years.
References


