Dilatometric behavior and crystallographic characterization of Portland-polyurethane composites for oilwell high-temperature cementing applications

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A R T I C L E   I N F O

Keywords:
Oilwell cementing
Portland cement
Polyurethane and thermal expansion

A B S T R A C T

In order to improve the behavior of Portland-based oilwell sheath to high-temperature applications and the corresponding thermal gradients, polymeric admixtures can be added. Steam injection, for instance, raises the cement sheath-steel casing interface temperature to ∼ 300 °C which can be deleterious to the mechanical stability and zonal isolation provided by the cement sheath as a result of cracking of the cement. Polyurethane can be added to the cement to improve its plastic behavior and reduce the thermal expansion mismatch between casing and sheath. However, the use polymeric admixtures, especially as aqueous dispersion, can affect the kinetics of the hydration reactions and, as a consequence, the crystallographic composition and coefficient of thermal expansion of the material. Therefore, the present study aimed at evaluating the effects of the addition of different concentrations of polyurethane on the thermomechanical properties of Portland cement pastes cured at 300 °C from 14 to 90 days. Formulations containing 1 gpc (0.052 kg), 2 gpc (0.102 kg) and 3 gpc (0.153 kg) of polyurethane, respectively named PU1, PU2 and PU3 were prepared according to the American Petroleum Institute guidelines. A standard PU-free slurry was also prepared. X-ray diffraction and dry dilatometric tests were carried out. The results revealed that the curing time does affect the kinetics of hydration of Portland-polyurethane composites, retarding the formation of high-temperature stable phases, i.e., tobermorite and xonotlite. Moreover, longer curing times were necessary to reveal the improved expansion of the composites with respect to the standard sample. The addition of polyurethane can be pointed as an approach to high-temperature oilwell cement applications, since it reduces the thermal mismatch between cement sheath and steel casing for and retards but do not prevent the formation of xonotlite.

1. Introduction

Thermal methods have been widely used worldwide to improve the production of heavy oils. Downhole heaters (Lund, 2003), in situ combustion (Zhao et al., 2015), injection of hot fluids, such as continuous (Pernites and Santra, 2016) or cyclic vapor injection (Ichim and Teodoriu, 2017) are some of the techniques used to reduce viscosity and enhance production. Cyclic vapor injection takes place in three stages, i.e., vapor injection, soaking, and production (Alvarez and Han, 2013). Vapor is usually injected at ∼ 300 °C, which can damage the naturally brittle cement sheath, either during injection or cooling, as a result of the thermal expansion mismatch between the cement sheath and steel casing. The typical thermal expansion coefficients of steel casings is about 13 × 10^-6 °C^-1 whereas that of oilwell cement is ∼ 9–10 × 10^-6 °C^-1 at the water-saturated state (Chougnet-Sirapian et al., 2011). Cracking and loss of adherence due to thermomechanical stresses affect both the mechanical integrity and zonal isolation of the well (Bu et al., 2017).

Increasing the coefficient of thermal expansion and improving the plastic behavior of cement pastes can be achieved by the addition of temperature-resistant plastic materials, such as lattices, including polyurethane (Artioli and Bullard, 2013; Jiang et al., 2016; Zhang and Sum, 2018; Souza et al., 2018).

The addition of polymeric admixtures to Portland cement is known to affect the kinetics of hydration (Kong et al., 2015; Jinhui et al., 2017), thereby extending the setting time and the formation of
crystalline phases responsible, for instance, for high temperature strength, as in the case of tobermorite and xonotlite. This can also have an effect on the thermal expansion behavior of cement pastes, as the presence of a latex in the mix affects moisture content, internal humidity, porosity and the development of cement hydration products (Bu et al., 2017).

Therefore, the objective of the present study is to evaluate the effect of the addition of different concentrations of polyurethane on the expansion behavior of Portland-polyurethane slurries hardened at 300 °C under pressure to simulate pumping conditions (3 kpsi). The crystallographic composition of the composites was evaluated by X ray diffraction. For high temperature applications, the cementing materials must develop strength values to overcome the retrogression effect. To that end, all compositions included 40% silica flour to assure the formation of the crystallographic phases responsible for high-temperature strength (Costa et al., 2017; Pernites and Santra, 2016). Literature on the dilatometric behavior of thermally-cycled Portland-polymer composites is scarce. The thermal expansion of hardened cement materials can be evaluated by conventional dilatometry, which allows real time monitoring of the dimensional changes that occur in a sample submitted to a thermal cycle, however under dry conditions (Bu et al., 2017). A standard polyurethane-free composition was also mixed and characterized under the same conditions to assess the changes in thermal mismatch resulting from the addition of polyurethane.

### Table 1

<table>
<thead>
<tr>
<th>Composition</th>
<th>Material (g)</th>
<th>w/c ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Cement</td>
<td>Silica (40%)</td>
</tr>
<tr>
<td>PU0</td>
<td>561.33</td>
<td>224.53</td>
</tr>
<tr>
<td>PU1</td>
<td>559.03</td>
<td>223.61</td>
</tr>
<tr>
<td>PU2</td>
<td>556.74</td>
<td>222.7</td>
</tr>
<tr>
<td>PU3</td>
<td>554.48</td>
<td>221.79</td>
</tr>
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Fig. 1. X-ray diffractograms of formulations (a) PU0, (b) PU1, (c) PU2 and (d) PU3 after curing for 14 days.
2. Materials and methods

Three Portland-polyurethane compositions were mixed containing 1, 2, and 3 gpc of polyurethane (PU1, PU2 and PU3) and cured after 14, 28 and 90 days. A standard slurry (PU0) was also prepared. All slurries included 40% silica flour to prevent retrogression. The samples were prepared to result in the final volume of 600 cm$^3$, necessary to perform all laboratory tests according to the American Petroleum Institute guidelines (Table 1) (Api, 2013).

The cement used was Portland Class A (CIMESA- Cimento Sergipe S.A., Laranjeiras, Brazil), industrially adjusted to replace the Portland class G cement, commonly used in oilwell cementing but not available everywhere. Silica flour, also from CIMESA, and PU W320 aqueous dispersion (Chemtura, São Paulo, Brazil) were also used.

Previous experience showed that the addition of polyurethane resulted in extensive foaming during mixing, therefore, an antifoam (VIAPOL, EUCLID GROUP) was included in the formulation. Water from the local supplier was used and the water-to-cement ratio was adjusted to achieve the same density for all compositions, i.e., 15.6 lb/gal (1.87 g/cm$^3$). All tests were performed according to Api (2013) except the dilatometric characterization.

A Chandler 80-60 mixer was used to prepare the samples. Polyurethane, Portland cement and silica flour were previously and manually mixed and then added to water, as the mixer rotated at 4000 ± 200 rpm. Addition took place during 15 s. The speed was then increased to 12000 ± 500 rpm during 35 s, and the mixer was turned off. The mixing protocol was established by the American Petroleum Institute (Api, 2013) to reproduce the mixing energy reached in field operations. After mixing, the slurries were poured into cylindrical metal molds (ϕ = 50 mm, h = 100 mm) and soaked in a thermostatic bath at 38 °C for 11, 25 or 87 days. At the end of each curing period, the samples were moved to a Chandler 1910 chamber and maintained pressurized at 300 °C under 3 kpsi (20,68 MPa) for 3 days for X-ray diffraction tests. Samples were ground down, dried in oven at 48 °C for 2 h and analyzed by XRD using a Bruker Eco D8 ADVANCE diffractometer operating at 1000 W. The range of $5° \leq 2\theta \leq 80°$ was scanned at 15 rpm using Cu Kα radiation and a Ni filter. A Netzsch DIL 402 PC apparatus under flowing Argon was used in the dilatometric analyses. Cylindrical 5 mm × 25 mm samples were demolded and maintained in room temperature for 2 h. The temperature range evaluated was from 30 °C to 300 °C. Two heating rates were examined, i.e., 2 and 10 °C/min. Each test was carried out three times.

3. Results and discussion

The formation of xonotlite, stable at high temperatures and

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![Image](https://via.placeholder.com/150)

**Fig. 2.** X-ray diffractograms of formulations (a) PU0, (b) PU1, (c) PU2 and (d) PU3 after curing for 28 days.
characterized by high Ca/Si ratio (Nelson and Guillot, 2006; Hidalgo et al., 2007) was noticed in all samples, regardless of the setting time or the presence of polyurethane (Figs. 1–3).

Polyurethane was not detected by XRD because of its amorphous nature. Small amounts of tobermorite were identified in all formulations containing polyurethane after curing for 14 days (Fig. 1), contrary to what was observed in the standard sample. Since xonotlite is a product from the modification of tobermorite (Pernites and Santra, 2016), which is predominant at temperatures below \( \sim 150 ^\circ C \), the presence of polyurethane as a polymeric film dispersed in the cement matrix, may have slowed down the kinetics of transformation of tobermorite into xonotlite. This can be confirmed by Figs. 2 and 3, where the crystallographic compositions of samples cured during 28 and 90 days showed no presence of tobermorite, fully converted into xonotlite.

The absence of tobermorite has been reported in cement formulations containing 40% silica without polyurethane, submitted to high temperatures curing cycles similar to those carried out herein (Pernites and Santra, 2016; Costa et al., 2017). Tobermorite and xonotlite have been identified upon studying the hydrothermal formation of calcium silicate. Both depict compact structures and good thermal stability. The higher stability of xonotlite has also been reported (Shaw et al., 2000). Synchrotron studies (Pernites and Santra, 2016) suggest a two-stage mechanism for the highly ordered crystal formation of either tobermorite or xonotlite from amorphous or partially crystalline C-S-H gel, taking place between \( \sim 150 ^\circ C \) and \( 310 ^\circ C \). At this dosage and curing condition, all the crystalline silica materials in the cement mixture are completely consumed in the reaction as show (Figs. 2 and 3), showing only peaks of xonotlite.

The effect of the heating rate on the dilatometric tests was examined (Fig. 4). The dilatometric profile was affected more significantly by the heating rate than the presence of polyurethane. The lower heating rate (2 °C/min) resulted in uniform distribution of temperature, which is especially important in materials with low thermal conductivity, which affects the evaluation of the coefficient of thermal expansion (Bu et al., 2017; Aleem et al., 2014; Shui et al., 2010). All tests were then performed at a heating rate of 2 °C/min.

The dilatometric behavior of the compositions investigated herein is shown in Fig. 5. The thermal expansion and contraction of hardened cement is a net result of the thermal expansion of the solid constituents and dehydration shrinkage through a complex network of pores distributed in the volume of the sample. As the temperature increases simultaneously with curing by hydration reactions, the liquid phase still present in the cement expands, resulting in an increase in the thermal expansion coefficient of the samples. This can be noticed by the non-

Fig. 3. X-ray diffractograms of formulations (a) PU0, (b) PU1, (c) PU2 and (d) PU3 after curing for 90 days.
linear expansion of the samples from room temperature to approximately 100–110 °C (Fig. 5a–c). All samples behaved in a similar manner regardless of the curing time. However, as shown in Fig. 5c, longer curing times resulted in increased expansion of PU1-PU3 samples compared to the standard sample (PU0) probably due to the consolidation of the polymeric film in the microstructure of the sample. From ~100 °C to 300 °C, all samples contracted and the coefficient of thermal expansion (CTE) values rapidly decreased as a result of the gradual loss of free water and from the main hydration products of the C-S-H gel. Garnier et al. (2008) pointed out that the CTE of cement is determined by moisture, internal humidity, porosity, and nature of hydration products. Under dry conditions, the effect of dehydration is predominant, and the CTE of the samples decreased. Bu et al. (2017) studied the thermal expansion/contraction behavior of oilwell cement with carbonaceous admixtures using dilatometry (heating rate of 1 °C/min), and observed similar behavior, i.e., shrinkage by dehydration ruling over thermal expansion.

The effect of polyurethane on the dilatometric behavior of the samples can be addressed comparing samples containing polyurethane with P0 in the range of 100–300 °C. The difference (dL/Lo)Pn - (dL/Lo)P0 at 300 °C, where n = 1, 2 and 3 is illustrated in Fig. 6. Positive values of (dL/Lo)Pn - (dL/Lo)P0 mean that the presence of polyurethane in the composition reduced the contraction of the sample compared to that of the standard sample. After curing for 14 days, samples PU1 and PU2 contracted less than the standard sample, contrary to what was observed for sample PU3. However, as curing continued (28 and 90 days), sample PU3 behaved likewise, confirming that the dilatometric behavior of Portland-polyurethane composites is affected by the kinetics of hydration of the C-S-H gel. Therefore, the addition of relatively high contents of polyurethane to Portland cement is beneficial to reduce the thermal mismatch between cement sheath and steel casing, once the effect on the hydration kinetics is taken into consideration.

A summary of the coefficients of thermal expansion of all formulations calculated in the range from 30 to 300 °C is listed in Table 2. The evolution of the expansive behavior of formulations containing polyurethane can be noticed as the curing time increases.

4. Conclusions

The effect of the addition of an aqueous dispersion of polyurethane to class A Portland cement for oilwell applications was investigated. The addition of polyurethane delayed the formation of xonotlite by the transformation of tobermorite. Both are high-temperature stable phases important to prevent the retrogression of Portland-based materials at high-temperatures, such as those characteristic of vapor injection operations in oilwells. Mixtures of tobermorite and xonotlite were detected by X-ray diffraction in samples containing polyurethane and cured for 14 days. Longer curing times resulted in the sole presence of
Polyurethane-free samples depicted only the presence of xonotlite regardless of the curing time. The presence of polyurethane also affected the coefficient of thermal expansion of the materials, since its presence slows down the kinetics of hydration of the samples. As the concentration of polyurethane in the sample increased (sample PU1 to PU3), the expansion behavior characteristic of the polymer required longer curing times to become evident. Adding polyurethane to oilwell Portland cements used in high-temperature oilwell cements decreases the thermal mismatch between cement sheath and steel casing. In addition, it reduces the brittle behavior of the cement, overall contributing to the thermal mechanical behavior of the sheath material under submitted to high temperatures and gradients.

Acknowledgements

The Federal Institute of Education, Science and Technology of Rio Grande do Norte for licensing the corresponding author as well as the Cement Laboratory (LABCIM) and the Laboratory of Ceramics and Metals (LMCME) staff for all the support in the experimental development of this research.

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