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Effect of sugarcane biomass waste in cement slurries submitted to high temperature and pressure

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ABSTRACT

Cementitious materials are subjected to changes in their microstructure and mechanical behavior when submitted to high service temperatures. In the oil industry, Portland-based slurries are used where conditions imply high temperatures and high pressures, e.g., steam injection or recovery of heavy oils. The present study investigated the hydration behavior and mechanical strength of cement slurries containing sugarcane biomass waste or silica flour, submitted to high temperature and pressure cycles using a curing chamber. The slurries were initially cured for 28 days at 22 °C. After that, they were placed in a curing chamber for 3 days at 280 °C and 17.6 MPa. The results showed a decrease in the compressive strength of the slurries submitted to high temperature high pressure. The decrease in strength was less marked in the slurry containing 40% of sugarcane biomass waste, as a consequence of the formation of silica-rich phases, i.e., xonotlite and tobermorite. When the slurries were placed in the curing chamber at 280 °C and 6.9 MPa for 7 days (after initial curing for 14 days at 38 °C), the slurry containing 59% sugarcane biomass waste showed an increase in compressive strength, contrary to what was observed for all the other slurries tested.

1. Introduction

Cementitious materials submitted to high temperatures depict microstructural changes that ultimately result in loss of mechanical strength and increase in permeability. Both effects are deleterious to applications, such as oilwell cementing, where mechanical stability and zonal isolation are constantly required. The behavior of cementitious materials under high temperatures and high pressures is rather complex and affected by a series of parameters that include characteristics of the cement itself (particle size, hydration reactions, composition and porosity of the hardened phases) and of the environment (heating rate and humidity) [1,2]. The effect of the temperature on the mechanical strength of concrete affected by fire was studied and revealed mild loss of strength above 200 °C, but markedly above 400 °C [3,4]. This effect is progressive due to the loss of water chemically combined with C–S–H and sulfoaluminates at 180–300 °C, the decomposition of calcium hydroxide at 450–550 °C and the complete decomposition of C–S–H at 700–900 °C [5,6].

In the oil industry, Portland-based cement slurries are used to fill the annulus between the casing and the formations exposed to the wellbore. The main roles of the cement sheath are to provide mechanical stability and zonal isolation to the well [7]. Under geothermal conditions or due to the injection of steam to recover heavy oils, the static bottom hole temperature (BSHT) may exceed 120 °C, which is deleterious to the strength and durability of the cement sheath [8]. The formation and stability of hydrated calcium silicates at high temperatures and pressures are highly relevant to the strength and durability of the hardened slurries. Large amounts of Portlandite ($Ca(OH)_2$) and hydrated calcium silicate, both rich in calcium, in hydrated slurries is considered harmful, since they result in high permeability and low compressive strength [9].

Hydrated calcium silicate (C–S–H) is the main product of cement hydration. It is responsible for the strength of the cement in addition to having good stability at temperatures up to 110 °C. However, at higher temperatures, C–S–H converts into calcium-rich phases, a harmful transformation for the integrity of the cement [7,9,10].

The structure of C–S–H varies from semi-crystalline to highly crystalline. Crystalline C–S–H phases are formed at high temperatures whereas the semi-crystalline ones are formed upon hydration at ambient temperature [11,12]. Nevertheless, all possible C–S–H structures have yet to be determined. Any model that determines the structure of C–S–H must take into consideration that the Ca:Si ratio of the C–S–H phase present in commercial cement ranges

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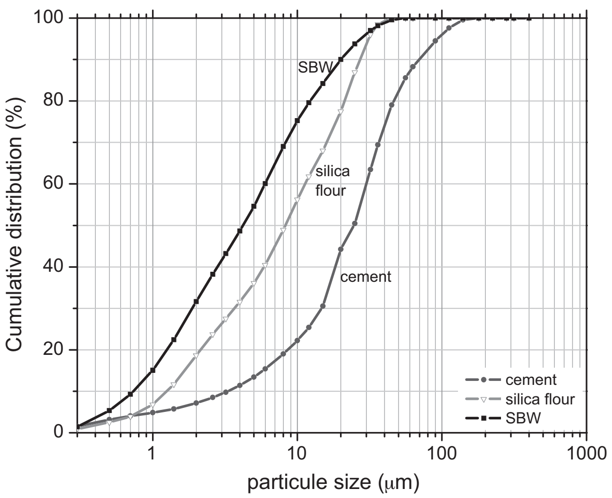

Fig. 1. Granulometric distribution of the materials.

between 0.7 and 2.3. Moreover, the composition of C–S–H becomes more homogeneous as the age of the cement advances. Finally, the C–S–H present in different types of cement shows significant amounts of substitute ions, the most common of which is Al^{3+} [12].

The addition of sugarcane biomass ash has been studied in building cement, mortar and concrete due to its high silica content and consequent potential as mineral additive and pozzolanic material [13–15]. This study investigates the effect of the addition of sugarcane biomass waste and silica flour on the formation of crystalline phases and the compressive strength of oilwell cement slurries submitted to high temperature and high pressure curing.

2. Experimental procedure

2.1. Materials

Type I Portland cement (PC) industrially modified to meet the property requirements for oil well cementing was used as base material in the prepartion of the slurries. Silica flour (SF), commonly used for high temperature oil well cementing, was added to a group of slurries to establish grounds for comparison. Sugarcane biomass waste (SBW), randomly collected during cleaning of the industrial boiler, was obtained after the electric energy cogeneration process of a local sugar and alcohol plant. The sugarcane biomass waste was milled to increase its reactivity and characterized. The collected waste was oven dried at 105 ± 5 °C then ground and dried for 3 h in a rotary ball mill. Fig. 1 shows the granulometric distribution of the waste obtained after milling along with those of the other materials used.

The chemical composition of the starting materials, determined by energy dispersive X-ray fluorescence (XRF) in a Shimadzu EDX-820 spectrometer is shown in Table 1.

The sugarcane waste and silica flour were also characterized by X-ray diffraction (Fig. 2) in a Shimadzu XRD-7000 diffractometer using CuKα radiation using 30 kV and 30 mA.

2.2. Slurry preparation and analysis

Slurries were formulated to reach densities from 1.87 g/cm^3 to 1.95 g/cm^3 using concentrations of sugarcane biomass of 10%, 20%, 30%, 40% or 59%. 40% silica flour was used and a reference slurry with no mineral addition was also prepared (Table 2).

The slurries were mixed using a Chandler 80-60 mixer, according to API Spec 10 [16]. Cubic test specimens with 5 cm edge were molded for each formulation and curing process. After molding, the test specimens were submitted to two different curing cycles (Fig. 3) using typical temperature and pressure oilwell conditions:

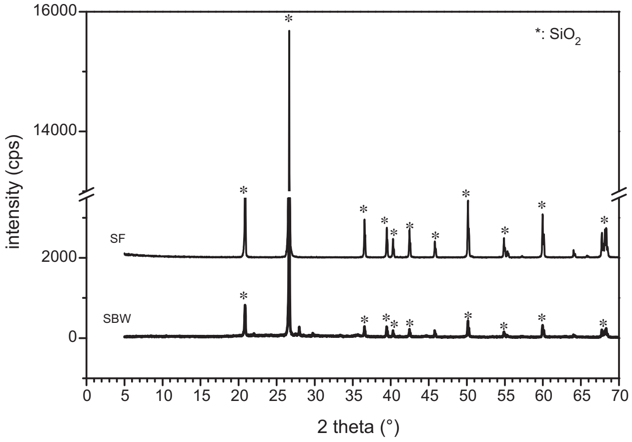

Fig. 2. XRD of SBW and SF.

Curing cycle 1 – Carried out for samples RS, SBW10, SBW20, SBW30, SBW40 and SF40. The samples were cured in thermal bath at 22 °C for 28 days. Three test specimens from each formulation were used for compression tests and 3 others were placed inside a pressurized chamber with oil at 280 °C and under 17.2 MPa for 3 additional days. These samples were also mechanically tested.

Curing cycle 2 – Carried out for samples RS, SBW40, SF40 and SBW59. The samples were cured in thermal bath at 38 °C for 14 days. Three test specimens from each formulation were used for compression tests and 3 others were placed inside a pressurized chamber with oil at 280 °C and under 6.9 MPa for 7 additional days, in a pressurized curing chamber. These samples were also mechanically tested.

All compressive strength tests were carried out using a Shimadzu AG-I testing machine. Samples were also analyzed by X-ray diffraction in a Shimadzu XRD-7000 diffractometer using CuKα radiation using 30 kV and 30 mA and scanning electron microscopy in a Philips modelo XL30 ESEM.

3. Results and discussion

3.1. Mechanical evaluation

Different concentrations of sugarcane biomass waste were added to evaluate its influence on the properties of slurries cured

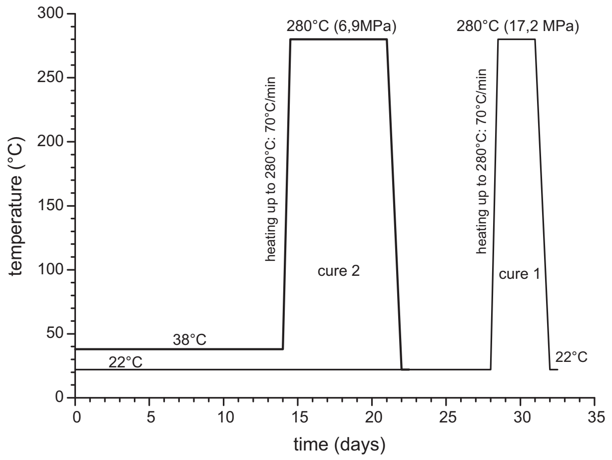

Fig. 3. Slurry curing cycles.

Table 1
Chemical composition (wt.%) of the starting materials.

	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	Na_2O	K_2O	CaO (free)
PC	20.17	4.60	3.15	61.76	3.52	2.84	0.17	0.90	1.93
SF	95.0	2.0	0.20	–	–	1.80	–	–	–
SBW	70.02	5.35	9.19	3.15	2.63	2.26	0.00	2.03	–

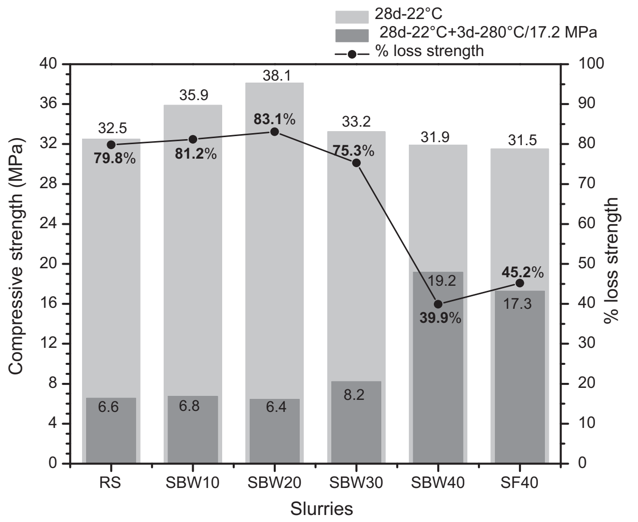

Fig. 4. Compressive strength of the cement slurries submitted to the first curing cycle.

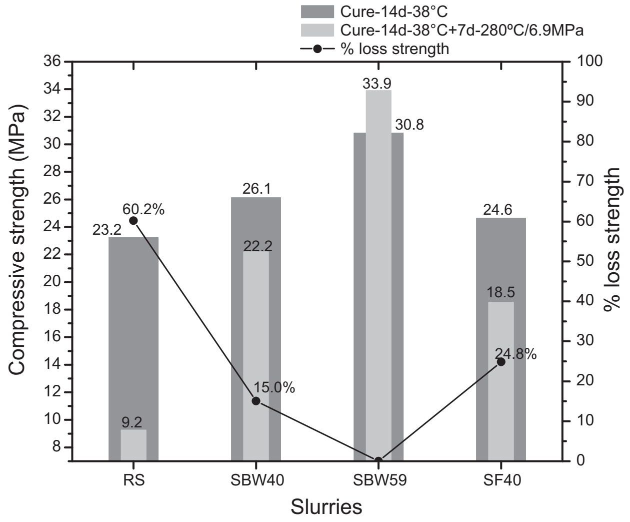

Fig. 5. Compressive strength of cement slurries submitted to the second curing cycle.

at high temperatures and pressures. The first curing high temperature and pressure curing cycle (280 °C and 17.2 MPa) caused retrogression of the compressive strength of all slurries analyzed, compared to those cured at 22 °C for 28 days (Fig. 4). This retrogression was more severe in the reference slurry (RS), SBW10, SBW20 and SBW30, resulting in loss of strength of 79.8%, 81.2%, 83.1% and 75.4%, respectively.

The slurry containing 40% sugarcane biomass waste (SBW40) showed higher compressive strength after curing at high temperature and pressure. The strength decreased by roughly 40% after such curing cycle, surpassing the performance of the slurry containing 40% silica flour (SF40), whose strength decreased by ∼45%. It should be pointed out that the SF40 sample was not expected to show retrogression, since this material is the most widely used one in oil wells submitted to high temperatures.

Compressive strengths of around 18 MPa (2600 psi) are able to withstand the mechanical forces generated in oilwells [17]. Therefore, only the SBW40 slurry could be used, since they depicted compressive strengths slightly above 19 MPa after exposure to high temperatures.

The second curing cycle of 14 days at 38 °C, followed by curing in oil at 280 °C under 6.9 MPa for 7 days was performed only for RS, SBW40 and SF40 samples. These slurries showed the best performance after the low-temperature step of the cycle. SBW59 samples were formulated to evaluate the effect of higher BWOC % contents of sugarcane waste in the slurry. The addition of 59% sugarcane waste, maintaining the water:cement ratio at 0.46, increased the density of the slurry and the need for a larger amount of dispersant to mix the components. However, in terms of cement consumption, SBW59 slurry represents a decrease of 40% compared to the reference slurry, whereas SBW40 slurry contains only 24% less cement than the reference slurry.

The incorporation of 59% waste, maintaining the water:cement ratio at 0.46 increased the density of the slurry and the need for a larger amount of dispersant to produce the mixture. Fig. 5 shows the compressive strengths of these slurries after the high-temperature step of the curing cycle. It can be observed that a higher concentration of the sugarcane waste and a smaller water:cement ratio is essential to prevent strength retrogression. This is due to the lower CaO : SiO_2 ratio in the formulation, in addition to the smaller amount of evaporable water in the slurry, lowering the internal pressures of gaseous products capable of decomposing the slurry.

3.2. *Microstructural characterization*

The marked decrease in compressive strength with an increase in temperature and pressure, observed in samples RS, SBW10, SBW20 and SBW30 is related to the high CaO : SiO_2 ratio of the anhydrous mixture of cement and silica flour or sugarcane waste. This leads to the conversion of hydrated calcium silicate

Table 2
Slurry compositions.

	BWOC (%)	Density (g/cm^3)	PC (g)	SBW (g)	SF (g)	Water (g)	Dispersant (g)	Antifoam (g)	Water/cement
RS	0	1.87	772.00	–	–	353.89	–	1.34	0.46
SBW10	10	1.87	710.58	71.06	–	338.71	0.74	1.24	0.48
SBW20	20	1.87	662.46	132.49	–	323.4	2.07	1.15	0.49
SBW30	30	1.87	620.68	186.20	–	311.03	2.59	1.08	0.50
SBW40	40	1.87	583.85	233.54	–	300.13	3.05	1.02	0.51
SF40	40	1.87	559.93	–	224.0	334.65	2.04	0.97	0.60
SBW59	59	1.95	463.2	308.80	–	212.33	3.87	1.20	0.46

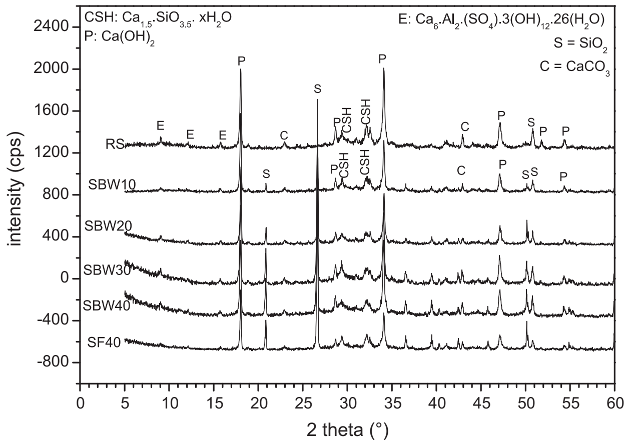

Fig. 6. XRD of slurries after curing for 28 days at 22 °C.

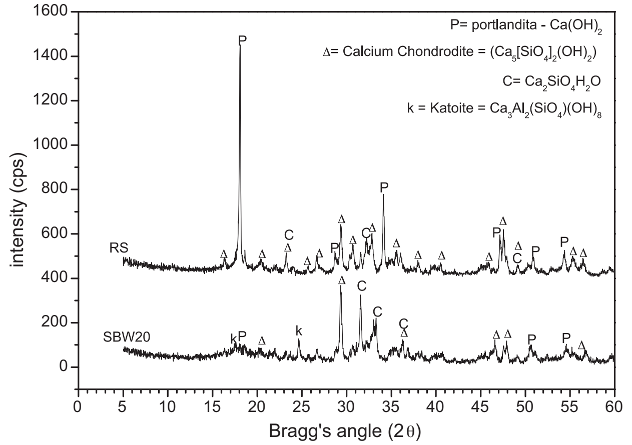

Fig. 7. XRD of the reference slurries and SBW20 after curing at 22 °C for 28 days and 280 °C for 3 days.

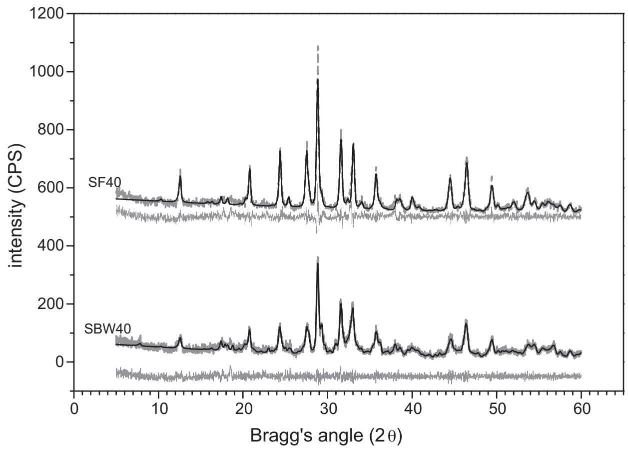

Fig. 9. Refined XRD of samples SBW40 and SF40 after curing cycle 1 at high temperature.

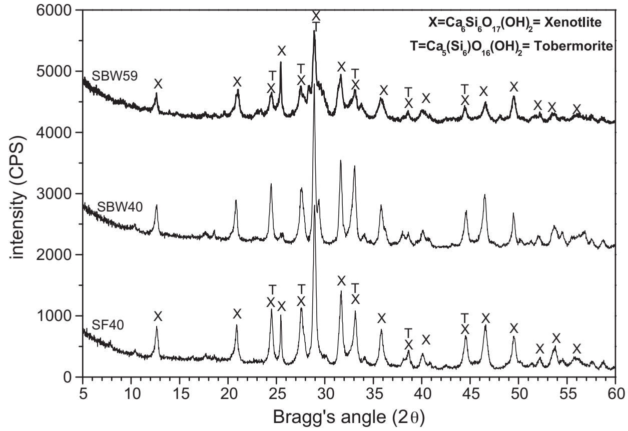

Fig. 10. X-ray diffractograms of the slurries after the 2nd curing cycle at high temperature.

($Ca_{1.5} \cdot SiO_{3.5} \cdot xH_2O$), found in these hydrated slurries at low temperatures, into silicates such as $Ca_2 \cdot SiO_4 \cdot H_2O$ and $Ca_5 \cdot (SiO_4)_2 \cdot (OH)_2$, which are calcium-rich phases, with Ca:Si ratio in C–S–H of 2.5 and 2.0, respectively. This can be observed in the X-ray diffractograms of the slurries cured at 22 °C and 280 °C (Figs. 6 and 7).

$Ca_5 \cdot (SiO_4)_2 \cdot (OH)_2$ is similar to reinhardbraunsite, which has a Ca:Si ratio of 2.5. This phase was also found upon studying the hydration of beta-calcium silicate submitted to high temperatures [18].

The slurry containing 20% sugarcane waste and submitted to high temperature (curing cycle 1) depicted the katoite phase, which is not found in the reference slurry, in addition to nearly total consumption of calcium hydroxide. This confirms the reaction between sugarcane waste and Portlandite at high temperature and

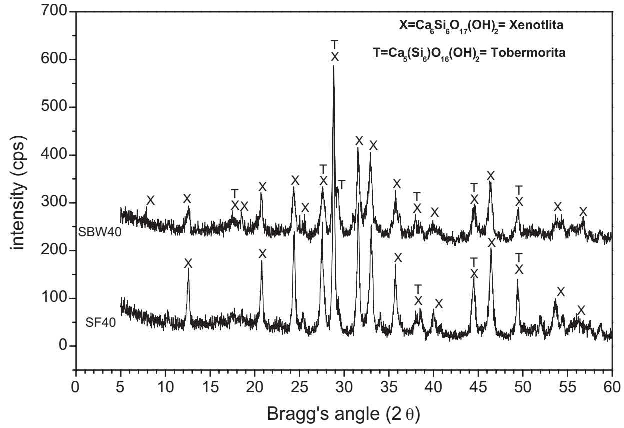

Fig. 8. XRD of SBW40 and SF40 after curing at 22 °C for 28 days and 280 °C for 3 days.

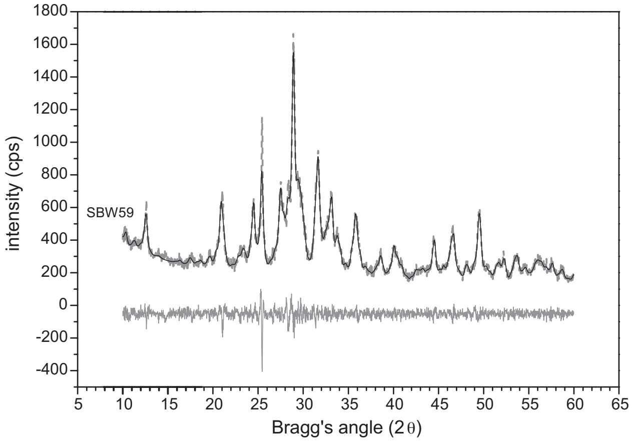

Fig. 11. Refined XRD results of the SCB59 cement slurry after the 2nd curing cycle at high temperature.

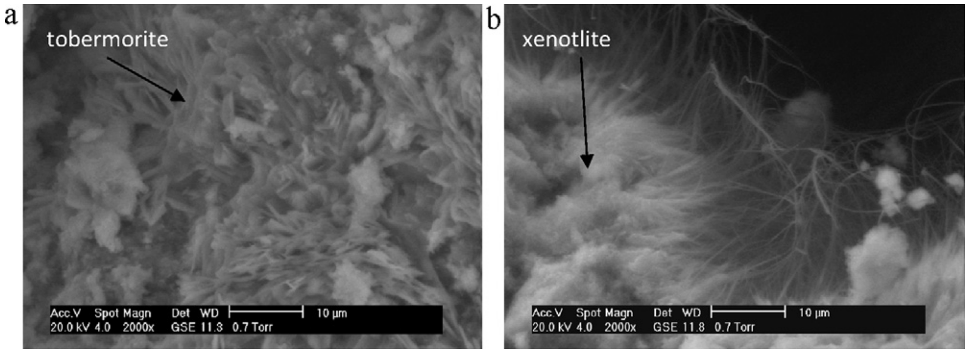

Fig. 12. SEM of SBW40 after curing at high temperature.

pressure, as well as the activation of the aluminate phase present in the waste, which determined the formation of katoite, which consists of calcium, alumina and silica ($Ca_3 \cdot Al_2 \cdot (SiO_4) \cdot H_2O$).

A significant change was observed in the hydration products formed in the SBW40 and SF40 samples, when submitted to high temperatures, as revealed in the X-ray diffractograms shown in Fig. 8. The hydration products formed in these slurries are the calcium silicate hydrates xonotlite ($Ca_6 \cdot Si_6O_{17} \cdot (OH)_2$) and tobermorite ($Ca_5 \cdot Si_6O_{16} \cdot (OH)_2$), which is a highly crystalline hydrated calcium silicate, formed only when the $CaO:SiO_2$ ratio of the anhydrous slurry is less than or equal to 1.0 and the temperature is above 110 °C. These hydration products are responsible for maintaining the compressive strengths of the hardened slurry.

Ca:Si ratios of tobermorite and xonotlite are 0.83 and 1, respectively. These phases were also found in oilwell slurries with silica flour, submitted to high temperature from the onset of hydration [9,19], suggesting that the SBW40 slurry can also be used in primary cementing of high temperature high pressure wells, and not just in steam injection wells, where slurries are only needed at high temperatures after complete cement hydration.

The Ca:Si ratio of C–S–H varies from 1.2 to 2.5 for hydrated slurries. However, this ratio may be less than 1 when mineral particles are added to the cement slurry [12], as confirmed in the present study.

The diffractograms of samples SBW40 and SF40 were refined by the Rietveld method. The results are plotted in Fig. 9. In the SBW40 slurry, 76.6% of the hydration products corresponded to xonotlite and 23.4% to tobermorite. The correlation coefficient between the experimental results and the refined data is 1.15. The SF40 sample contained 64.1% of the hydration products for xonotlite and 35.9% for tobermorite with a correlation coefficient of 1.16. At 280 °C, the hydration products are nearly totally converted into xonotlite, leaving tobermorite as a minor phase.

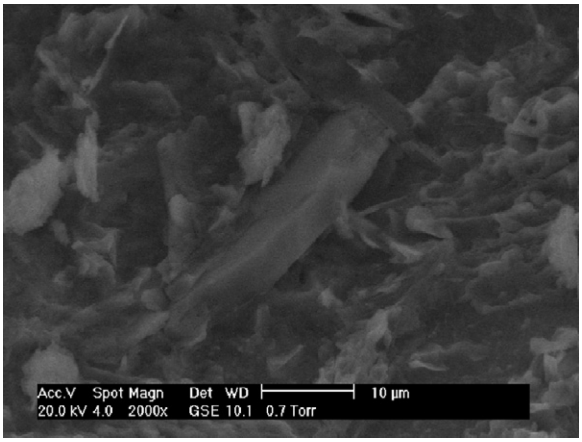

Fig. 13. SEM of RS after curing at 22 °C.

The hydration products of the slurries containing silica after the second curing cycle are the same as those obtained after the first curing cycle at high temperature and pressure (Fig. 10).

The refined X-ray diffractogram of sample SBW59 is shown in Fig. 11. The volume of the xonotlite and tobermorite phases was 38.5% and 61.5%, respectively, corresponding to an increase in sugarcane waste content.

Fig. 12 shows a SEM image of the hydrated SBW40 slurry, after curing cycle 1. The structure of the slurry predominantly consisted of tobermorite and xonotlite. The morphologies observed confirmed those shown elsewhere [10]. Tobermorite and xonotlite are denser than $Ca_{1.5} \cdot SiO_{3.5} \cdot xH_2O$ (CSH), encountered in the reference slurry cured at 22 °C, as it can be seen in Fig. 13, where the presence of calcium hydroxide is still noticed.

4. Conclusions

The first curing cycle at 22 °C for 28 days followed by 280 °C for 3 days resulted in a decrease in strength in all slurries analyzed. The most marked reductions were in the slurries without addition of silica followed by those with 10%, 20% and 30% sugarcane waste.

The slurry containing 40% sugarcane waste (SBW40) showed the lowest loss in strength (39.9%), maintaining a compressive strength of 19.2 MPa, exceeding that of the slurry containing silica flour (SF40), which was 17.3 MPa. These findings demonstrate the potential of sugarcane biomass waste as a substitute for silica flour in oil well cements submitted to high temperatures.

The hydration analysis of slurries containing 40% sugarcane waste and 40% silica flour submitted to the first curing cycle at high temperature revealed the presence of silica-rich phases such as xonotlite and tobermorite, with Ca:Si ratios of 1 and 0.83, respectively. These phases were responsible for maintaining the compressive strength of the hardened slurry. Refined X-ray diffractograms also showed that the slurry with 40% sugarcane waste contained 76.6% of the hydration products for the xonotlite phase and 23.4% for the tobermorite phase.

In the second curing cycle, sample SBW40 exhibited strength retrogression of only 15%, whereas the SF40 sample lost 25% of its strength. These losses were lower than in the first cycle due to the accelerated hydration reactions between the hydration products of the slurry and the silica present in the additions, resulting from the high temperature at the onset of slurry hydration (14 days).

The second curing cycle confirmed the potential of sugarcane waste to prevent retrogression, since the SBW59 sample showed an increase in compressive strength after this curing cycle at high temperature and pressure. This finding is related to the larger amount of silica available and the lower water:cement ratio of the slurry, leading to the presence of xonotlite and tobermorite.

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