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Hydration of oil well cement containing sugarcane biomass waste as a function of curing temperature and pressure



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ABSTRACT

The present study evaluates hydration of oil well cement containing sugarcane biomass waste. Thus slurries were cured at low temperature (22 °C) and ambient pressure for 28 days. Additional curing at high temperature (280 °C) and high pressure (17.2 MPa) for 3 days was evaluated. Slurries containing 10–40% by weight of cement were evaluated by thermogravimetry, X-ray diffraction, compressive strength and permeability. The results revealed that sugarcane biomass waste reacts with calcium hydroxide present in cement slurries. Slurries containing 20% of the residue and cured at 22 °C for 28 days depicted the reduction of ~49.9% of the calcium hydroxide content. The addition of 40% SBW and curing at 22 °C for 28 days and 280 °C/17.2 MPa for 3 days yielded the transformation of common C–S–H into silica-rich C–S–H. Sugarcane biomass waste can replace the silica flour as an additive for oil well cement, resulting in improved compressive strength and permeability of the slurries.

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1. Introduction

Brazil is the world's leading producer of sugarcane, with the production to be estimated as 719.1 million tons in 2010 (Hofsetz and Silva, 2012). After the sugarcane is crushed, the remaining fibrous bagasse is used as biomass in cogeneration, finally resulting in large amounts of residues. The composition of such residues mainly consists of silica, either amorphous or crystalline (Martirena et al., 2006; Frías et al., 2007; Cordeiro et al., 2008), which implies a potential application in concrete, mortars and cement slurries (Cordeiro et al., 2009; Sales and Lima, 2010; Anjos et al., 2011).

The pozzolanic reaction between sugarcane biomass waste (SBW) and calcium hydroxide (Ca(OH)₂) results in hydrated products, such as calcium silicate hydrate (C–S–H) and is highly dependent on the chemical composition and particle size distribution of the SBW and the curing temperature.

The formation of hydrated products in cement slurries begins within the first hours after the addition of water and practically ends after 360 days. However, the age of reference to evaluate

cement hydration is normally 28 days. At this point, 70–80% of the hydration products are already formed and subsequent hydration is much slower.

Differential thermal analysis (DTA) is likely the best method to determine the calcium hydroxide content of a hydrated cement slurry, since the decomposition of calcium hydroxide is well defined and takes place between 425 and 550 °C (Taylor, 1997).

Thermal analyses (TG/DTG/DSC) have also been used by a number of researchers to determine the amount of water chemically combined with the hydrated products of cement slurries, based on mass loss, thereby obtaining an indirect measure of the degree of cement hydration (Yogendran et al., 1991; Dweck et al., 2002; Vedalakshmi et al., 2003).

The thermogravimetric analysis has been well established as a useful tool to assess the hydration of cement slurries cured at temperatures up to 60 °C (Bhatty and Reid, 1985; Knapen et al., 2009; Zhang et al., 2010; Esteves, 2011;). The calculation of the total hydration and contents of calcium hydroxide may for individual slurry result in distinct values as a function of the method used; however, it can be used to compare slurries with different compositions, since all methods are based on total mass loss, which is related with the total hydration and mass losses corresponding to the different hydrated products. The thermogravimetric evaluation of the hydration of ordinary Portland cement cured at temperatures

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ranging from 100 to 800 °C has been reported elsewhere (Alonso and Fernandez, 2004; Alarcon-Ruiz et al., 2005).

The present study aimed at evaluating the hydration of cement slurries containing sugarcane biomass waste cured at 22 °C for 28 days at ambient pressure. The effect of an additional curing period of 3 days at 280 °C/17.2 MPa was evaluated.

2. Experimental procedure

2.1. Materials

Special Portland cement (PC) was used in the production of the slurries, consists of Portland cement for cementation of oil wells, according NBR 9831 (ABNT, 2006). Silica flour (SF) is commonly used with special Portland cement for cementing operations above 110 °C and was chosen as control material.

Sugarcane biomass waste (SBW) was obtained from a local sugar/alcohol mill (Arez, Brazil). The residue was collected from the cogeneration boilers and ball-milled for 3 h at a ratio of 1 kg SBW:10 kg milling balls.

Particle size, chemical composition and XRD patterns corresponding to SBW, SF and cement can be found elsewhere (Anjos et al., 2011). TG/DTG plots corresponding to Portland cement, silica flour and the sugarcane biomass waste are all shown in Fig. 1.

The mass loss of the sugarcane biomass waste is 18.9% between 313 °C and 575 °C, and is associated with the decomposition of its organic constituents (hemicellulose, cellulose and lignin).

2.2. Methods

Cement slurries with additions of SBW from 10% to 40% BWOC (by weight of cement) were prepared along with a composition containing 40% silica flour as well as a reference slurry (RS) with no SBW or silica flour (Table 1), to achieve uniform density of

1.87 kg/dm³ (15.6 lb/gal) in the fresh state. The slurries were mixed using a Chandler 80–60 mixer, according to API SPEC 10 (2000). Dispersant and antifoaming agents were used to adjust the rheology of the system and prevent gas entrapment, respectively.

After mixing, nine cubic samples (5 × 5 × 5 cm³) of each composition were molded and cured:

Curing 1: Low temperature—Carried out for samples RS, SBW10, SBW20, SBW30, SBW40 and SF40. Curing in thermal bath at 22 °C for 7 and 28 days. Compressive strength, permeability, DRX and TG/DTG analyses were carried for each formulation after 7 and 28 days.

Curing 2: High temperature—Carried out for samples RS, SBW20, SBW40 and SF40. Three test specimens for each formulation were cured in thermal bath at 22 °C for 28 days followed by three additional days in a oil pressurized chamber at 280 °C under 17.2 MPa.

Thermogravimetry analyses were carried out in a Shimadzu TGA-50 thermobalance under nitrogen atmosphere with a flow rate of 50 mL/min and heating rate of 10 °C/min, at a temperature range between 20 °C and 1000 °C.

X-ray diffraction patterns were collected in a Shimadzu XRD-7000 diffractometer using Cu K α radiation, voltage of 30 kV and current of 30 mA.

Permeability was determined in Core Lab permeameter using nitrogen gas.

3. Results and discussion

The thermogravimetric plots of the slurries cured at 22 °C for 7 and 28 days are shown in Figs. 2 and 3, respectively. The loss of mass between room temperature and 105 °C is due to unbound water evaporation. The mass loss between 20 °C and 70 °C corresponds to the evaporation of water present in the pores larger than 0.05 μ m. Between 70 and 105 °C, water from capillary pores is released.

The temperature range at which hydrated products lose chemically combined water when submitted to thermal analyses varies as a function of the age of the cement, water-to-cement ratio and addition of SBW, as it can be seen in the DTG plots shown in Figs. 2 and 3b.

Dehydration occurred between 105 and 460 °C due to loss of water chemically combined with all hydrated phases present in the slurry, including ettringite and hydrated calcium silicate, which are only present in the cement slurries, as shown in XRD (Fig. 4). The mass loss associated with these hydration products is in good agreement with values reported elsewhere (Alonso and Fernandez, 2004; Giergiczny, 2006). Decarbonation took place between 600 and 700 °C and dehydroxylation of Ca(OH)₂ between 460 and 520 °C.

Decreases in mass losses were observed with respect to calcium hydroxide for all slurries with SBW compared to the reference slurry and the slurry containing silica flour, indicating the pozzolanic activity of SBW after 7 and 28 days of hydration.

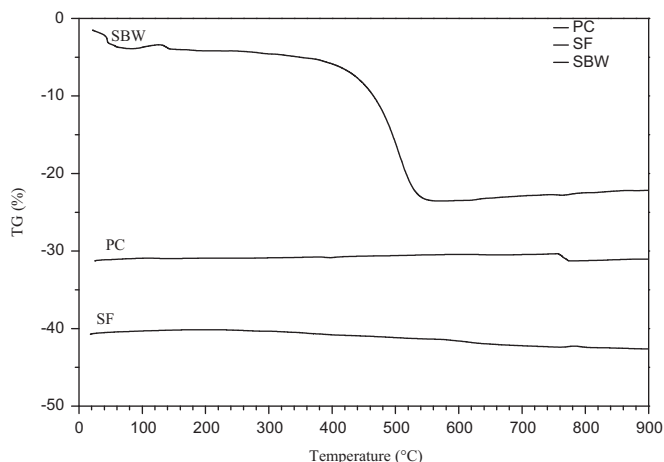


Fig. 1. TG/DTG plots of Portland cement, silica flour and the sugarcane biomass waste.

Table 1
Slurry compositions.

Slurry	Cement (g)	BWOC (%)	SBW (g)	SF (g)	Water (g)	Dispersant (g)	Antifoaming (g)	Water/cement
RS	772.00	0	–	–	353.89	–	1.34	0.46
SBW 10	710.58	10	71.06	–	338.71	0.74	1.24	0.48
SBW 20	662.46	20	132.49	–	323.40	2.07	1.15	0.9
SBW 30	620.68	30	186.20	–	311.03	2.59	1.08	0.50
SBW 40	583.85	40	233.54	–	300.13	3.05	1.02	0.51
SF 40	559.93	40	–	223.97	334.65	2.04	0.97	0.60

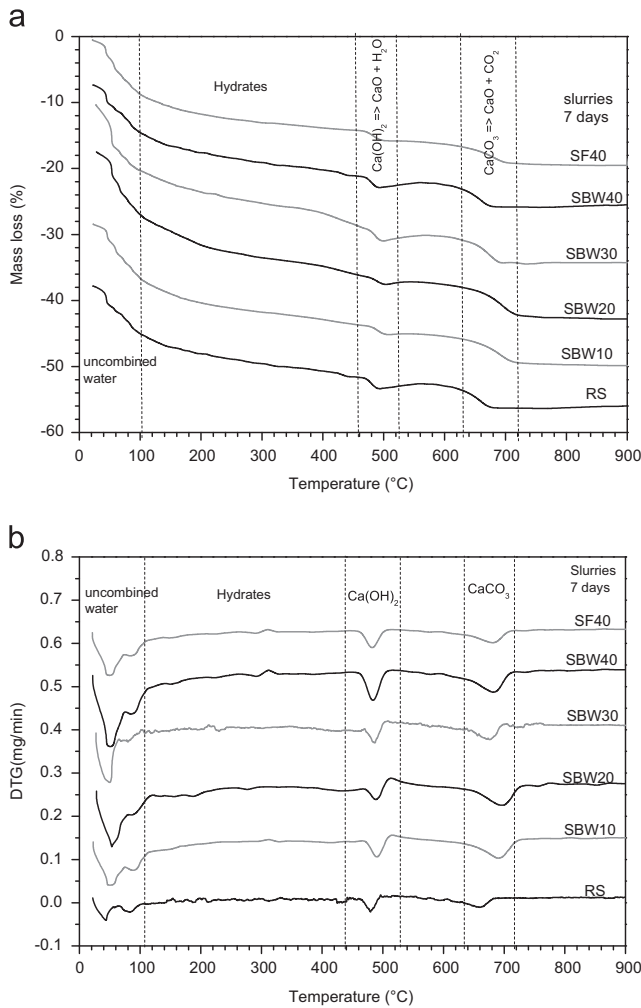


Fig. 2. (a) TG and (b) DTG plots of cement slurries after 7 days of curing.

The addition of SBW decreased the mass loss of the slurry with respect to calcium hydroxide (CH) after curing. Mass losses associated to Ca(OH)_2 decomposition, CH_{free} and Ca(OH)_2 content after curing at 22 °C for 7 and 28 days are shown in Table 2. The free calcium hydroxide (CH_{free}) formed during the hydration of cement slurries was determined by Eq. (1_ (Taylor, 1997; Knapen, et al., 2009), where WL is the mass loss seen in the TG plots and MW is the molecular weight. The percentage of calcium hydroxide ($\text{CH}[\%]$) present in the slurries was calculated as being the ratio of CH_{free} to total hydration (chemically combined water).

$$\text{CH}_{\text{free}} [\%] = \text{WL}_{\text{Ca(OH)}_2} [\%] \times \frac{\text{MW}_{\text{Ca(OH)}_2}}{\text{MW}_{\text{H}_2\text{O}}} \quad (1)$$

The maximum consumption of Ca(OH)_2 was observed for the slurry containing 20% SBW. The reduction in Ca(OH)_2 content in the slurries cured for 28 days compared to the reference slurry was 34.7%, 49.9%, 30.4% and 21.4% for SBW10, SBW20, SBW30 and SBW40 slurries, respectively. The reduction for the slurry containing silica flour (40SF) was 30.6%.

The reduction in Ca(OH)_2 present in the cement slurries containing SBW is also evidenced by the decrease in the Ca(OH)_2 peaks in the X-ray diffraction patterns of the hydrated slurries (Fig. 4).

The slurries containing 10% and 20% SBW exhibited higher compressive strengths after 28 days, as shown in Fig. 5. The increased compressive strength of slurries containing SBW is associated with the reduction in the contents of Ca(OH)_2 , in addition to a decrease

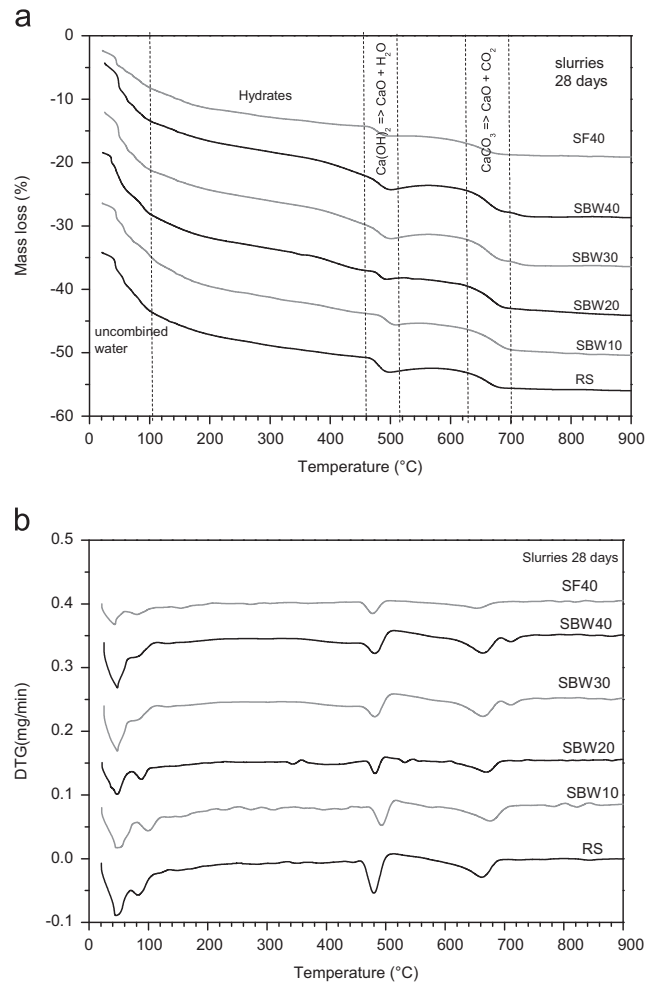


Fig. 3. (a) TG and (b) DTG plots of cement slurries after 28 days of curing.

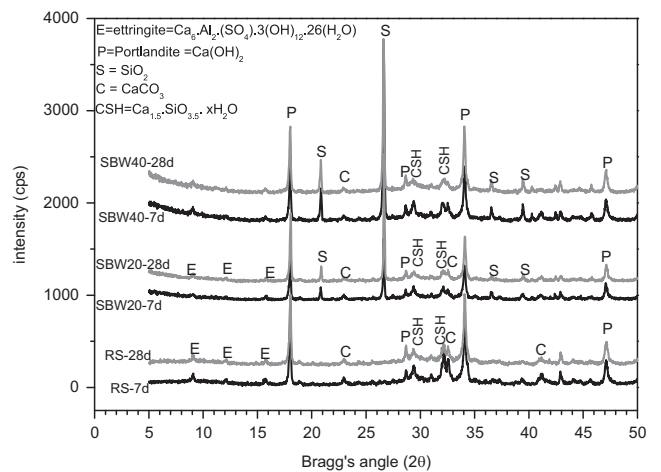


Fig. 4. XRD of RS, SBW20 and SBW 40 slurries after curing for 7 and 28 days at 22 °C.

in the porosity of slurries with SBW, due to the filler effect of unreacted SBW.

The presence of SBW contributes to the lower permeability of hardened cement samples, as shown in Fig. 6. Such a reduction in permeability is related to the refinement of the cementitious matrix, filling of the pores by unreacted SBW particles and the

Table 2
Mass loss and calcium hydroxide content.

Slurry	Free water (%)		Dehydroxylation Ca(OH) ₂ (%)		Total mass loss (%)		CH _{free} (%)		CH (%)	
	7d	28d	7d	28d	7d	28d	7d	28d	7d	28d
RS	7.46	9.51	1.64	2.30	17.73	21.74	6.76	9.44	11.67	16.78
SBW10	8.68	9.62	1.30	1.59	21.45	23.89	5.36	6.55	9.00	10.98
SBW20	10.56	9.95	1.08	1.25	25.31	25.68	4.43	5.15	7.60	8.40
SBW30	10.17	9.22	1.74	1.76	23.84	24.27	7.14	7.24	12.45	11.68
SBW40	7.60	7.87	1.45	2.09	21.04	22.55	5.98	8.59	9.36	13.19
SF40	8.76	8.53	1.51	1.56	19.03	19.03	6.2	6.43	11.49	11.65

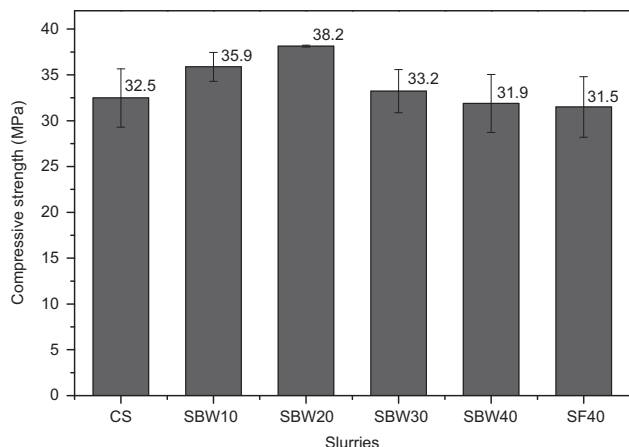


Fig. 5. Compressive strength of the cement slurries after curing for 28 days at 22 °C.

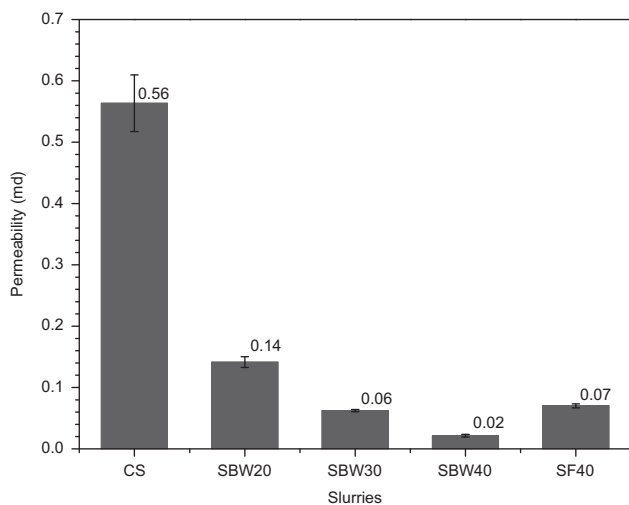


Fig. 6. Permeability of cement slurries after curing for 28 days at 22 °C.

pozzolanic reaction between SBW and calcium hydroxide present in the hydrated slurries.

The thermogravimetric plots of cement slurries labeled RS and SBW20 cured at high temperature are shown in Figs. 7 and 8 along with the corresponding low-temperature plots. As it can be seen, the events that took place at high temperature are quite different than those established at low temperature regarding the mass loss of hydrated products such as C–S–H, hydroxide and calcium carbonate.

The change in the shape of the thermogravimetric plots (Figs. 7 and 8) is associated with transformations of the hydrated products as the slurries are cured at high temperatures. X-ray diffraction data revealed that slurries RS and SBW 20% depicted the transformation of C–S–H ($\text{Ca}_{1.5} \cdot \text{SiO}_{3.5} \cdot x\text{H}_2\text{O}$) to calcium-rich C–S–H ($\text{Ca}_2 \cdot \text{SiO}_4 \cdot \text{H}_2\text{O}$ and $\text{Ca}_5 \cdot [\text{SiO}_4]_2 \cdot (\text{OH})_2$), accompanied by a significant reduction in the contents of calcium hydroxide and suppression of ettringite, as shown in XRD (Fig. 9).

The thermal events related to the dehydration of C–S–H and dehydroxylation of $\text{Ca}(\text{OH})_2$ taking place in slurry RS-HT are shifted to high temperatures, i.e., 150–480 °C and 480–520 °C with respect to slurry RS-LT, 105–460 °C and 460–520 °C, respectively, for C–S–H and $\text{Ca}(\text{OH})_2$. This suggests different values of enthalpy for these compounds after thermal exposure.

Slurry SBW20-HT depicted continuous mass loss from 150 to 520 °C, related to the dehydration of C–S–H. The decomposition of calcium hydroxide was not noticed because of its reaction with SiO_2 and Al_2O_3 present in the SBW, which results in the formation of calcium silicates and silico-aluminates, such as chondrodite ($\text{Ca}_5 \cdot (\text{SiO}_4)_2 \cdot (\text{OH})_2$) and kaotite ($\text{Ca}_3 \cdot \text{Al}_2 \cdot (\text{SiO}_4) \cdot (\text{OH})_8$), as suggested by X-ray diffraction.

The thermogravimetric plots corresponding to slurries SBW40% and SF40% are shown in Fig. 10 and 11. These slurries were cured under high pressure and high temperature. Three events can be noticed and associated with the hydrated phases xenotlite and tobermorite. Their crystallization was established by X-ray diffraction, as reported elsewhere (Anjos et al., 2011). Xenotlite and tobermorite are C–S–H phases with Ca:Si equal to 1 and 0.83, respectively, as shown in XRD, Fig. 9. They are commonly found in SiO_2 -rich cement slurries with low CaO:SiO₂ cured under high pressure and high temperature (Nelson, 1990; Luke, 2004).

Tobermorite has been associated to mass losses between 60 and 260 °C (Klimesch et al., 2002), which is in good agreement with the range of 120–247 °C, observed herein. Moreover, the contents of tobermorite in slurries SBW40 and SF40, estimated by the ratio between the mass loss in this range and the mass loss of chemically combined water, are 26.6% and 34.5%, respectively. These values are quite close to the ones calculated using the Rietveld refinement of X-ray diffraction data reported elsewhere, i.e., Anjos et al. (2011).

These results combined to those of X-ray diffraction and compressive strength (Anjos et al., 2011) for the same formulations demonstrate the potential of sugarcane biomass waste as interesting mineral component of cement slurries cured at 22 °C and 280 °C/17.2 MPa.

4. Conclusions

The pozzolanic activity of fine sugarcane biomass waste (SBW) was confirmed by TG/DTG analyses of cement slurries containing SBW. The thermogravimetric method proved to be highly efficient

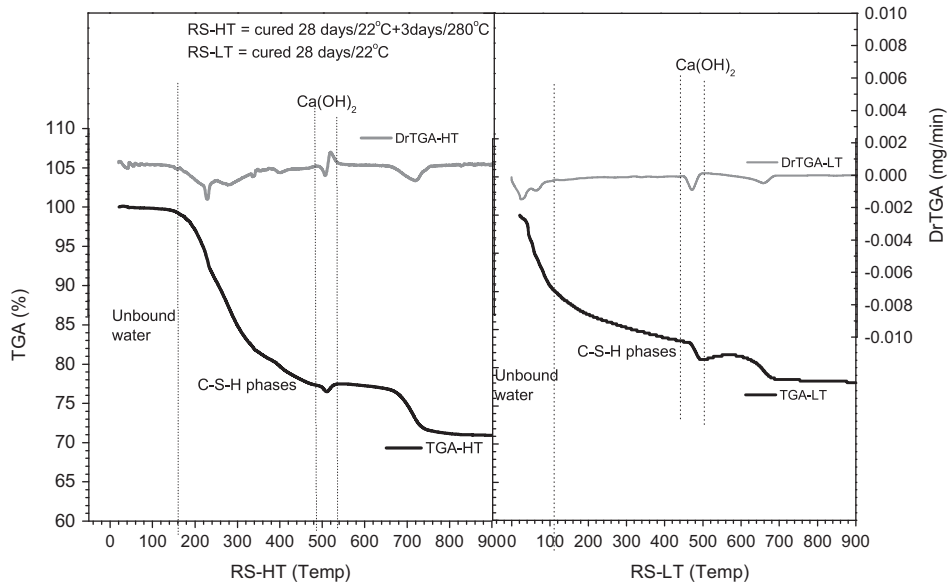


Fig. 7. TG/DTG curves of cured RS slurry.

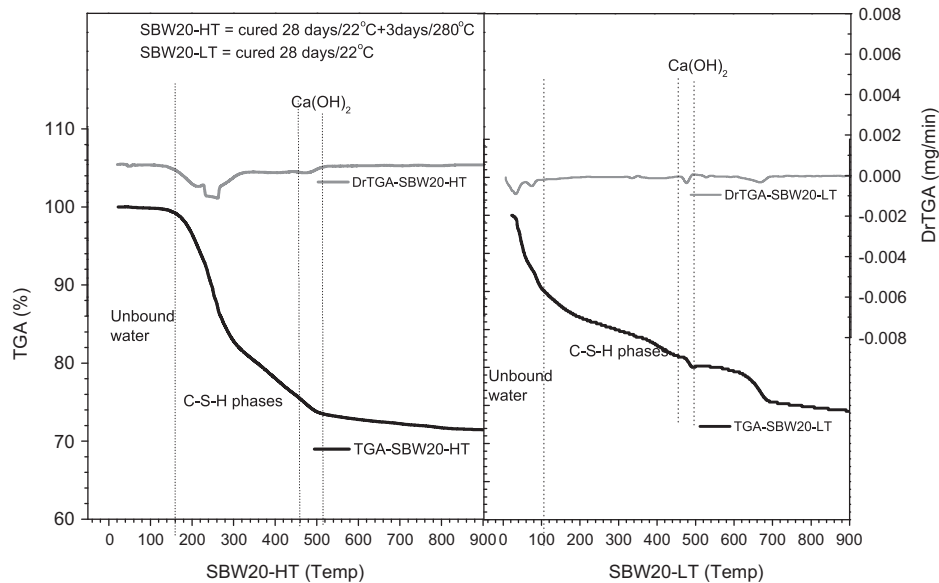


Fig. 8. TG/DTG curves of cured SBW20 slurry.

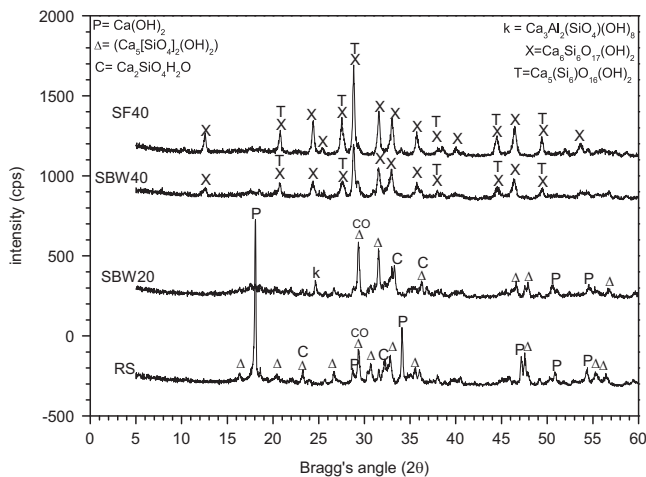


Fig. 9. XRD of RS, SBW20, SBW40 and SF40 slurries after curing for 28 days at 22 °C + 3 days at 280 °C/17.2 MPa.

in evaluating the hydration of cement slurries with mineral additives. Moreover, it is possible to quantify the decrease in calcium hydroxide contents present in the hydrated slurries.

The cement slurries containing SBW showed a significant reduction in the contents of calcium hydroxide in the range of concentrations evaluated (10–40% BWOC). The use of 20% SBW reduced the calcium hydroxide content to 49.9% as compared to the reference slurry.

The addition of SBW improved the compressive strength and reduced the permeability as compared the reference slurry and SF40.

TG/DTG plots of slurries cured at low temperatures are different than those of the same slurries cured at high temperatures and pressure, since different crystallographic phases, xenotlite and tobermorite, are formed under these conditions. The contents of tobermorite in the slurries containing 40% SBW and SF cured at high temperature and pressure were estimated by TG/DTG and are in good agreement with calculated using the Ritveld refinement of X-ray diffraction data.

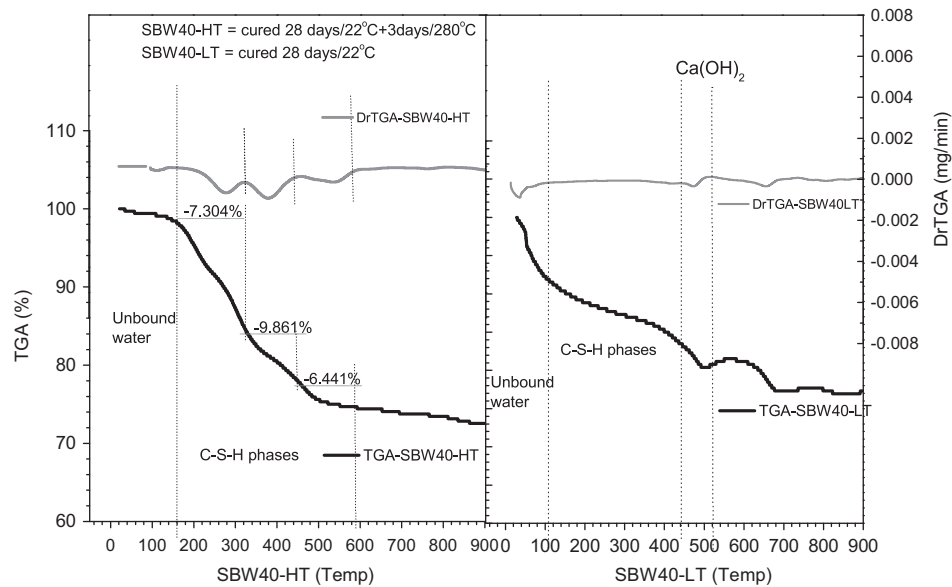


Fig. 10. TG/DTG curves of cured SBW40.

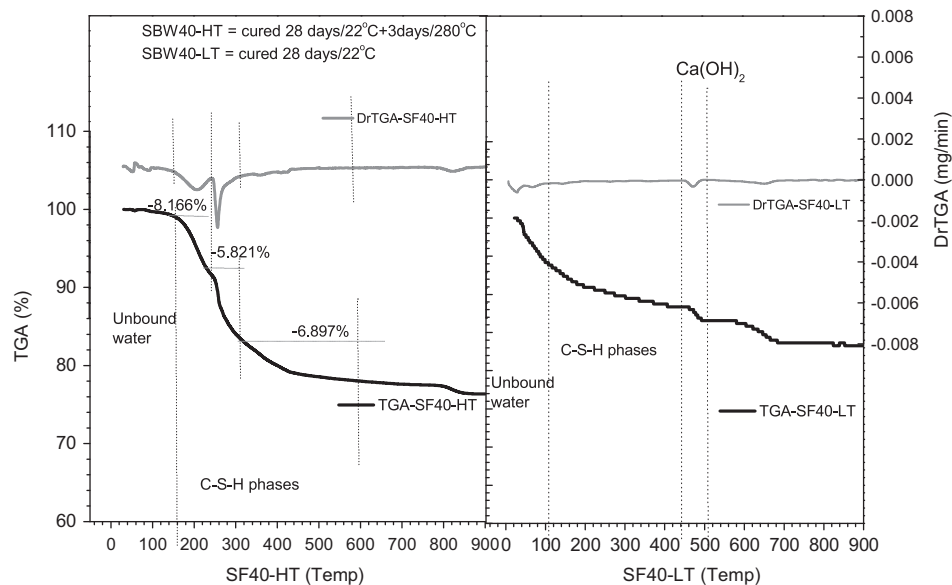


Fig. 11. TG/DTG curves of cured SF40 slurry.

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