# Influence of microwave oven calcination on the pozzolanicity of sugar cane bagasse ashes (SCBA) from the cogeneration industry

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## HIGHLIGHTS

- Microwave oven calcination improves the pozzolanic reactivity of SCBA.
- This also gives a reduction in the energy consumption needed to obtain SCBA with pozzolanic reactivity.
- The use of SCBA is promoted as a replacement for Portland cement.
- This enables environmental and economic improvements to be made in the construction industry.
- Agroindustrial by-products can be valorised in this way.

## ABSTRACT

This study evaluates the effects of microwave oven calcining conditions on the pozzolanicity of sugar cane bagasse ashes (SCBA) generated by the electric power cogeneration industry. The calcining temperatures varied between 600°C and 800°C, and the permanence times were 60 minutes in an electric oven and 30, 45 and 60 minutes in a microwave oven. To evaluate the behaviour of the ashes according to different calcining conditions, we carried out the following

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analyses: granulometric distribution (laser diffraction), oxide percentages (XRF), loss on ignition (LOI), powder X-ray diffraction (XRD), pozzolanic reactivity, determination of amorphous silica content and thermogravimetry of hydrated lime pastes (DTG). The results show that SCBA calcination in a microwave oven results in ashes with greater pozzolanic reactivity and a significantly more efficient burning process than in an electric oven.

Keywords: Microwave oven calcination, Sugar cane bagasse ash, SCBA, Cogeneration ashes, Pozzolanic materials, Energy efficiency.

## 1. Introduction

The Brazilian sugar-alcohol industry generates approximately four million tons of ash annually from the burning of sugarcane bagasse for the cogeneration of electric power using boilers. Several studies have shown that the sugarcane bagasse ash (SCBA) has a chemical composition that is suitable for use as a pozzolanic mineral additive, due mainly to its high silica content [1-10]. In addition, SCBA has little environmental impact, since it is a by-product that has a zero $CO_2$ emission balance; it is therefore an alternative to environmentally appropriate binders, and can minimise the negative environmental effects of Portland cement production [11-12].

However, inefficient burning conditions in the boilers in Brazilian plants (at temperatures below 800ºC) result in ashes with high levels of organic/carbonaceous material [13-15]. To reduce the amount of organic material and increase the amorphous silica content of SCBA, several researchers have proposed a methodology using electric oven calcination, at temperatures of around 700ºC and a minimum calcining time of one hour. This treatment requires high energy consumption, and this has prevented the widespread commercial use of this material [16-20].

In this context, a microwave oven is a suitable alternative, and can reduce both the burning time and the energy consumption of SCBA calcination. A microwave oven has several advantages over an electric oven, such as faster, more selective and more homogeneous heating

and higher energy efficiency (due to the shorter burning times and lower temperatures used) [21-26]. It can also be easily incorporated into the industry for ash calcination [27-29].

Ashes such as SCBA, which contain elevated levels of organic carbon-based material, show strong potential for microwave oven calcining, since carbon materials have high microwave absorption [30-34]. However, few studies have reported the use of a microwave oven in the calcination of agroindustrial ashes [35-40]. The most detailed study found in the literature [35] analysed the calcination of rice husk ash in a microwave oven at temperatures above 800ºC for 45 minutes, which resulted in ash with high levels of cristobalite and quartz. Further investigation is therefore needed of the effects of microwave oven calcining conditions (such as calcining time and temperature) on the properties of agroindustrial ashes, especially in terms of pozzolanicity activity.

Given the high efficiency of microwave oven calcination for materials rich in carbon, lower temperatures and shorter calcining times are expected, which can reduce the organic material content of the ashes when compared to an electric oven. Faster ash calcination processes with temperatures of between 600ºC and 700ºC [17-20] may also increase the likelihood of preserving silica with lower crystallinity.

We therefore investigate the effects of microwave oven calcining conditions on the pozzolanicity of SCBA generated by the electric power cogeneration industry, giving reactive ashes with low energy consumption.

## 2. Material and Methods

### *2.1. Materials*

SCBA was supplied by a sugar factory in Pirassununga, Sao Paolo, Brazil, as a product of bagasse burning in an electricity power cogeneration system. The SCBA was collected in October, since the harvest at this time of year has the lowest incidence of quartz contamination of the sugarcane bagasse, due to the low precipitation in the Pirassununga region. During the rainy

season, the wet soil adheres to the sugar cane plants during harvesting, increasing the quartz contamination of the bagasse. This SCBA was dried at 100°C ± 5°C for 24 h, and was homogenised using hand mixing. The CH:SCBA pastes and aqueous suspensions used in pH/electrical conductivity tests were produced using calcium hydroxide (Panreac S.A., 95% purity).

*2.2. Methods*

*2.2.1. SCBA calcination*

The temperature and calcining time were controlled to enable us to analyse the effects of microwave oven calcination on the pozzolanicity of SCBA. The SCBA was calcined using both a microwave oven (MWO) and an electric oven (EO). The electric oven was a Jung (model 10013) with 7000 W power, while the microwave oven had a frequency of 2.45 GHz and a power of 1400 W. We used a burning chamber of size 200 $cm^3$, with silicon carbide plates and electronic temperature control. In both types of ovens, the ratio between SCBA and burning chamber volume was kept constant at 0.04 for all calcining treatments.

The calcining temperatures were 600°C, 700°C and 800°C [17-20], and the permanence time at the calcining temperature was 60 minutes in the electric oven and 30, 45 and 60 minutes in the microwave oven [35]. Calcining times of below 30 minutes were disregarded, since preliminary studies showed that the loss on ignition (LOI) was too high for these calcining times. The heating rate was 4°C/min for the electric oven and 50°C/min for the microwave oven. In all cases, the ashes were removed immediately following calcining and cooled at room temperature (25°C ± 2°C). The SCBA calcination treatments are referred to here as EO*x* and MWO*x*-*t* (where *x* = 600°C, 700°C, 800°C and *t* = 30, 45, 60 minutes).

*2.2.2. Material characterisation*

Following calcination, the ash was ground for 30 minutes using a vibratory Micro Mill

Pulverisette 0 (Fritsch Industrie) with a volume of 200 $cm^3$ and a grinding ball of sintered corundum (diameter 50 mm, mass 370 g). The fineness of the ash was analysed using a laser diffraction particle size analyser (LDA), a Malvern (model Mastersizer 2000), and isopropyl alcohol as a non-reactive liquid. Morphological characterisation of the SCBA was performed using a Fesem Ultra 55 by Zeiss, while chemical characterisation was carried out using X-ray fluorescence (XRF) with a PANalytica MiniPal4. X-ray diffraction (XRD) analyses of SCBA were conducted using a Brucker AXS D8 Advance with CuKα radiation, from 10° to 60° (2θ), at 40 kV and 20 mA, using a step angle of 0.02° and a 2 s counting period.

*2.2.3. Evaluation of pozzolanic reactivity*

A method proposed by Tashima et al. [41] was used to evaluate the influence of the calcining conditions on the pozzolanicity of the SCBA. This method evaluates the pozzolanic reaction by monitoring CH:pozzolan aqueous suspensions in different proportions for seven days using pH and electrical conductivity measurements.

In this method, suspensions are saturated with an excess of solid calcium hydroxide. The reductions in the values of pH and electrical conductivity over the test period indicate the degree of unsaturation of the suspension relative to calcium hydroxide, due to the progress of the pozzolanic reaction; more specifically, this is due to the reaction between $Ca^{+2}$ and $OH^-$ ions dissolved in the water and pozzolan particles, forming stable and insoluble products [42].

Various CH:SCBA mass ratios (ranging from 1:9 to 4:6) were used, in which the total mass of solid was constant at 1.0 g in 50 mL of deionised water. The reactivity of the suspensions was analysed at temperatures of 40°C, 50°C and 60°C over seven days (168 hours).

To maintain homogeneity and to control the test temperature of the suspensions, a shaking water bath (Julabo SW22) operating in a temperature range of 20°C–99.9°C was used. A pH meter (Crison micro PH2001) and an electrical conductivimeter (Crison micro CM2201) were used to monitor the progress of the pozzolanic reaction.

128 *2.2.4. Determination of amorphous silica in SCBA*

129 The influence of the calcining process on the amorphous silica content of the SCBA was
130 evaluated following the procedures set out in the standards UNE 80225:1993 [43] and UNE-EN
131 196-2:1996 [44]. These procedures specify that the percentage of amorphous silica (also referred
132 to as reactive silica) contained in pozzolans is determined by the difference between the total
133 amount of silica and the silica that remains unchanged in the form of an insoluble residue after
134 the 4M hydrochloric acid reaction and 4M potassium hydroxide boiling, for an extraction time of
135 four hours. However, since Payá et al. [45] have shown that four hours of extraction is a very
136 aggressive approach that dissolves both amorphous and crystalline silica, and have suggested an
137 extractive treatment with 4M KOH for 3 min, we therefore used this length of time in the present
138 work.

139

140 *2.2.5. Analysis of lime fixation by thermogravimetry*

141 A thermogravimetric analyser (Mettler-Toledo TGA 850) was used to perform thermal
142 decomposition experiments (DTG) at a heating rate of 10°C/min from 35°C to 600°C in an $N_2$
143 atmosphere. Sealed aluminium crucibles of volume 100 µL with a pinholed lid were used for this.
144 Hydrated lime/pozzolan pastes were prepared with CH:SCBA ratios of 1:1 and 1:2 (by mass),
145 maintaining a water–solid ratio of 0.8. These pastes were analysed after seven and 28 days of
146 curing at 23°C at a relative humidity (RH) of 100%. To prepare the samples for TGA analysis, the
147 pastes were ground with acetone, filtered and put in an oven at 60°C for 30 min. Finally, the
148 samples were sifted using an 80 µm sieve.

149

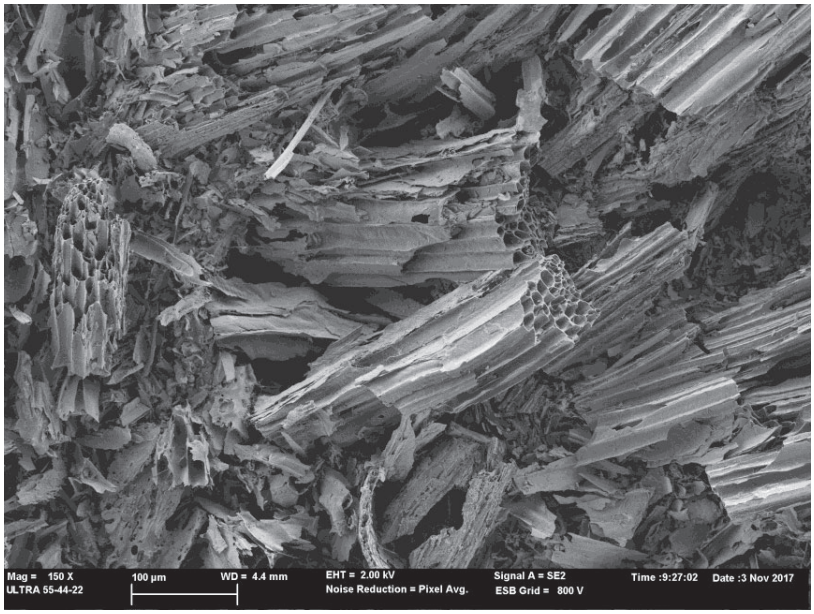
150 **3. Results**

151 The SCBA had a high carbon content, with an LOI value of about 80% (Table 1); this can be
152 attributed to the inefficiency of the burning process in the boilers, which generated a high
153 proportion of unburned SCBA. This can also be seen in the morphology of the originally received

SCBA, as illustrated in Fig. 1. Table 1 shows that there is a reduction in LOI values with an increase in the temperature of calcination in both the electric and microwave ovens. The calcining temperatures used were sufficiently high to reduce the organic/carbonaceous material in the ash by a substantial amount (to less than 6.10%). Figs. 2 and 3 show the ash morphology after calcination. The microwave oven was more efficient than the electric oven in terms of reducing LOI values [33-34]; in the electric oven, the LOI value decreased to 6.10% of its original value after one hour at 600º, while only 30 minutes were necessary to reduce the LOI to 4.20% in the microwave oven. Treatment at 800ºC in the microwave oven for 60 minutes reduced the LOI to 1% of its original value.

**Table 1.** Chemical composition of SCBA and LOI in mass percentage (%)

| Oxides (%) | As received | Electric Oven | | | Microwave Oven | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | 600°C | 700°C | 800°C | 600°C | | | 700°C | | | 800°C | | |
| | | | | | 30 min | 45 min | 60 min | 30 min | 45 min | 60 min | 30 min | 45 min | 60 min |
| $SiO_2$ | 7.74 | 37.45 | 38.56 | 38.76 | 38.21 | 38.25 | 38.76 | 39.00 | 38.96 | 39.00 | 39.32 | 39.36 | 39.48 |
| CaO | 3.23 | 15.63 | 16.10 | 16.18 | 15.95 | 15.96 | 16.18 | 16.28 | 16.26 | 16.28 | 16.41 | 16.43 | 16.48 |
| $Fe_2O_3$ | 1.80 | 8.72 | 8.98 | 9.02 | 8.89 | 8.90 | 9.02 | 9.08 | 9.07 | 9.08 | 9.15 | 9.16 | 9.19 |
| $Al_2O_3$ | 0.95 | 4.59 | 4.73 | 4.76 | 4.69 | 4.69 | 4.76 | 4.78 | 4.78 | 4.78 | 4.82 | 4.83 | 4.84 |
| $K_2O$ | 1.55 | 7.49 | 7.71 | 7.75 | 7.64 | 7.65 | 7.75 | 7.80 | 7.79 | 7.80 | 7.86 | 7.87 | 7.89 |
| $SO_3$ | 1.06 | 5.14 | 5.29 | 5.32 | 5.24 | 5.24 | 5.32 | 5.35 | 5.34 | 5.35 | 5.39 | 5.40 | 5.41 |
| $P_2O_5$ | 1.23 | 5.95 | 6.13 | 6.16 | 6.07 | 6.08 | 6.16 | 6.20 | 6.19 | 6.20 | 6.25 | 6.25 | 6.27 |
| MgO | 1.22 | 5.91 | 6.08 | 6.11 | 6.03 | 6.03 | 6.11 | 6.15 | 6.15 | 6.15 | 6.20 | 6.21 | 6.23 |
| $TiO_2$ | 0.38 | 1.82 | 1.87 | 1.88 | 1.85 | 1.85 | 1.88 | 1.89 | 1.89 | 1.89 | 1.91 | 1.91 | 1.91 |
| $V_2O_5$ | 0.06 | 0.27 | 0.28 | 0.28 | 0.28 | 0.28 | 0.28 | 0.28 | 0.28 | 0.28 | 0.28 | 0.29 | 0.29 |
| MnO | 0.11 | 0.53 | 0.54 | 0.54 | 0.54 | 0.54 | 0.54 | 0.55 | 0.55 | 0.55 | 0.55 | 0.55 | 0.55 |
| Cl | 0.09 | 0.42 | 0.43 | 0.43 | 0.42 | 0.42 | 0.43 | 0.43 | 0.43 | 0.43 | 0.44 | 0.44 | 0.44 |
| **LOI** | **80.6** | **6.10** | **3.30** | **2.80** | **4.20** | **4.10** | **2.80** | **2.20** | **2.30** | **2.20** | **1.40** | **1.30** | **1.00** |
| Total | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 |

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168 **Fig. 1.** SEM-ES micrograph of as-received SCBA

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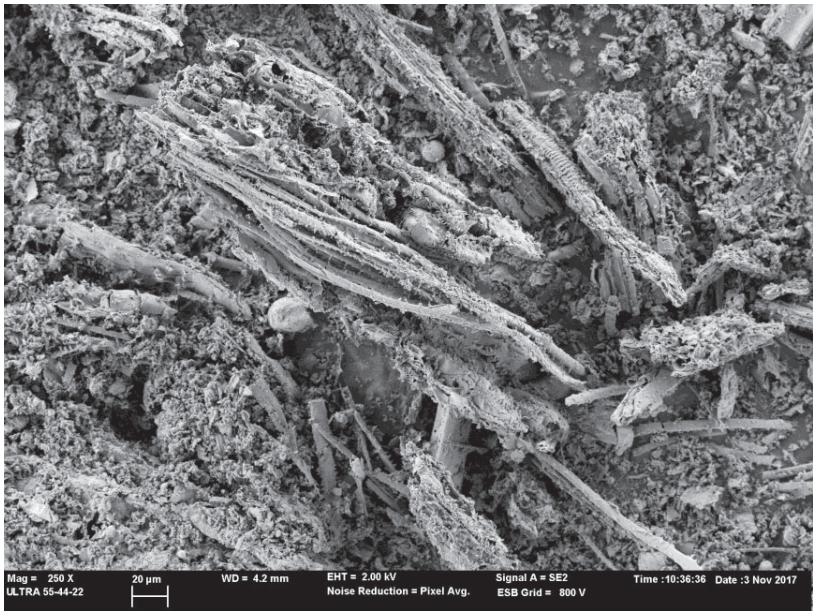


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171 **Fig. 2.** SEM-ES micrograph of SCBA calcined at 600ºC in an electric oven for one hour (EO600)

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**Fig. 3.** SEM-ES micrograph of SCBA calcined at 600ºC in a microwave oven for 30 minutes (MWO600-30)

$SiO_2$ is the main oxide present in the SCBA after the calcination treatments, with values in the range 37%–40% (Table 1). This is lower than the values observed in previous studies of Brazilian SCBA, which range between 50% and 80% [11-15]. This difference is probably due to the lower rate of contamination of quartz, since the SCBA was collected in October, a month that has a low rainfall in this region. Together, $SiO_2$, CaO, $Fe_2O_3$ and $Al_2O_3$ represent approximately 70% of the composition of the SCBA. Significant proportions of $K_2O$, MgO, $P_2O_5$ and $SO_3$ (around 5% and 7%) were also observed, as reported in other studies of Brazilian SCBA [14-19].

The ground SCBAs had similar particle size distributions (Table 2), with a mean particle size of between 14.38 and 17.11 µm. They also had similar values for D10, D50 and D90, which is important to prevent the particle size affecting the evaluation of the influence of the calcining treatments on the pozzolanic reactivity of the ashes [16].

**Table 2.** Particle size distribution of SCBA samples

| Calcining condition | $D_{med}$ (µm) | D10 (µm) | D50 (µm) | D90 (µm) |
|---|---|---|---|---|

| | | | | | |
|---|---|---|---|---|---|
| Electric oven 60 min | 600°C | 15.87 | 1.59 | 9.88 | 35.57 |
| | 700°C | 15.03 | 1.21 | 7.76 | 35.45 |
| | 800°C | 17.11 | 1.20 | 6.99 | 41.43 |
| Microwave oven 30 min | 600°C | 16.05 | 1.15 | 7.14 | 40.57 |
| | 700°C | 15.68 | 1.63 | 8.67 | 39.54 |
| | 800°C | 15.32 | 1.35 | 7.89 | 38.41 |
| Microwave oven 45 min | 600°C | 14.38 | 1.29 | 6.78 | 36.80 |
| | 700°C | 15.89 | 1.50 | 7.54 | 39.00 |
| | 800°C | 15.67 | 1.78 | 7.42 | 40.32 |
| Microwave oven 60 min | 600°C | 16.20 | 1.89 | 6.78 | 41.55 |
| | 700°C | 15.34 | 1.43 | 8.76 | 38.55 |
| | 800°C | 15.25 | 1.65 | 9.68 | 37.65 |

*$D_{med}$ = mean particle size; D10, D50 and D90 are the maximum sizes of particles making up 10%, 50% and 90% of the sample volume, respectively.

The XRD pattern for the as-received SCBA (Figure 4) indicates the presence of quartz (soil contamination), calcite and anhydrite. It also indicates the presence of a halo between 20° and 35° (2θ); this can be attributed to the presence of amorphous silica, which provides the SCBA with pozzolanic reactivity.

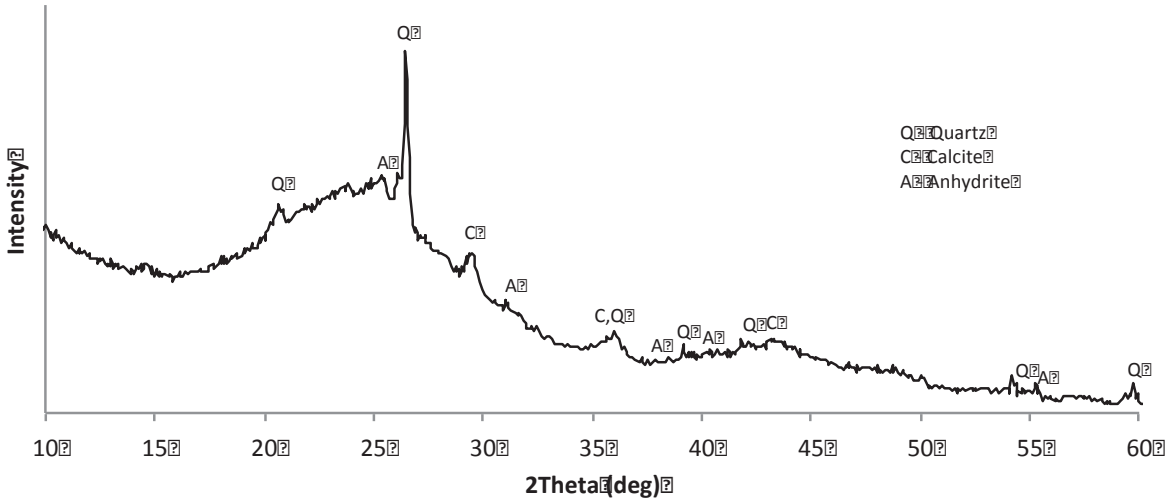



**Fig. 4.** XRD pattern for the as-received SCBA

Figures 5 and 6 present the XRD patterns for ashes calcined for one hour in an electric oven and in a microwave oven, respectively, at 600°C and 800°C. The XRD patterns show a remarkable difference between the calcined and as-received SCBA, indicating that the calcination

temperatures used in this research were efficient in terms of removing carbon and volatile compounds from the SCBA.

The diffractograms in Figures 5 and 6 demonstrate the presence of quartz ($SiO_2$), calcite ($CaCO_3$), forsterite ($Mg_2SiO_4$), several sulphates (anhydrite ($CaSO_4$), syngenite ($K_2Ca(SO_4)_2.H_2O$) and arcanite ($K_2SO_4$)) and phosphates (whitlockite ($(Ca,Mg)_3(PO_4)_2$) and $Ca_7Mg_2P_6O_{24}$ (derived from whitlockite)). This result is in alignment with the chemical composition of SCBA shown in Table 1 and reported in prior studies of Brazilian SCBA [19,46].

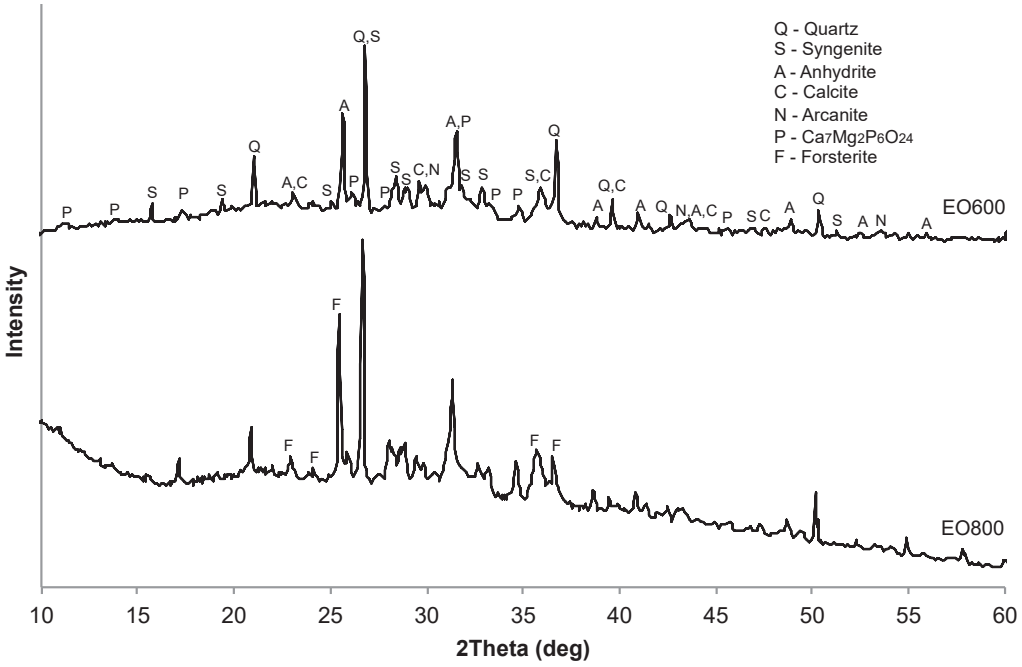



**Fig. 5.** XRD patterns for SCBA calcined at 600ºC and 800ºC in an electric oven for one hour (EO600 and EO800, respectively)

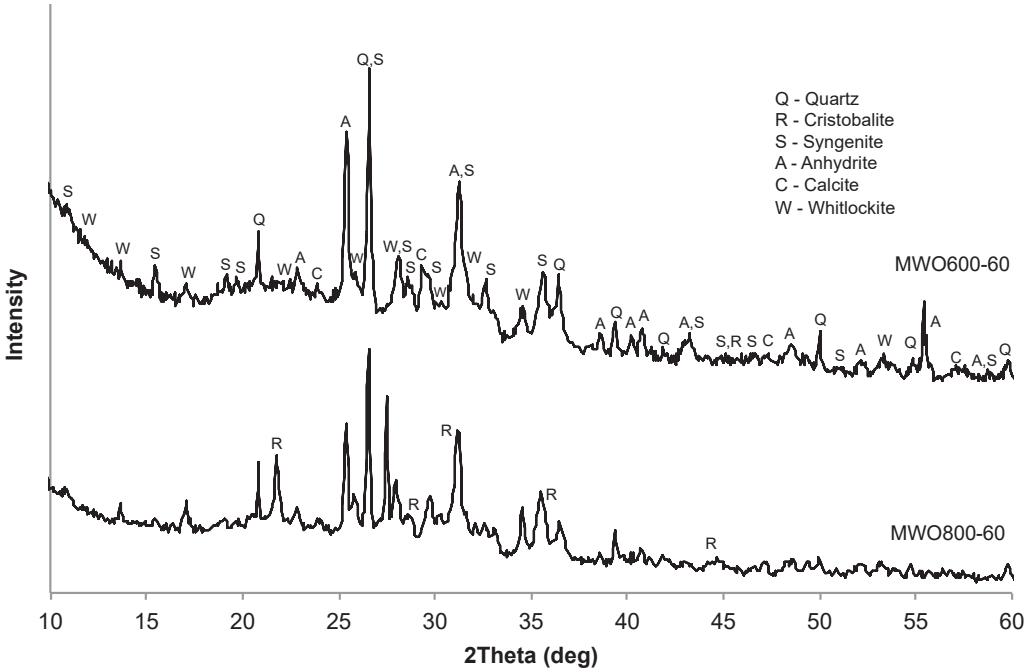



**Fig. 6.** XRD patterns for SCBA calcined at 600ºC and 800ºC in a microwave oven for one hour (MWO600-60 and MWO800-60, respectively)

Cristobalite, generated by the crystallisation of amorphous silica under certain heating conditions, was observed only in the ashes calcined for one hour in a microwave oven at 800°C (MWO800-60). Figure 7 shows the pattern in detail between 20° and 22.5° (2Theta) for treatments at 800ºC.

The results of X-ray analysis indicate that except for EO800 and MWO800-60, the treatments used were efficient in removing the organic matter without promoting the crystallisation of silica in the form of cristobalite or forsterite, both of which reduce the pozzolanic potential of ash.

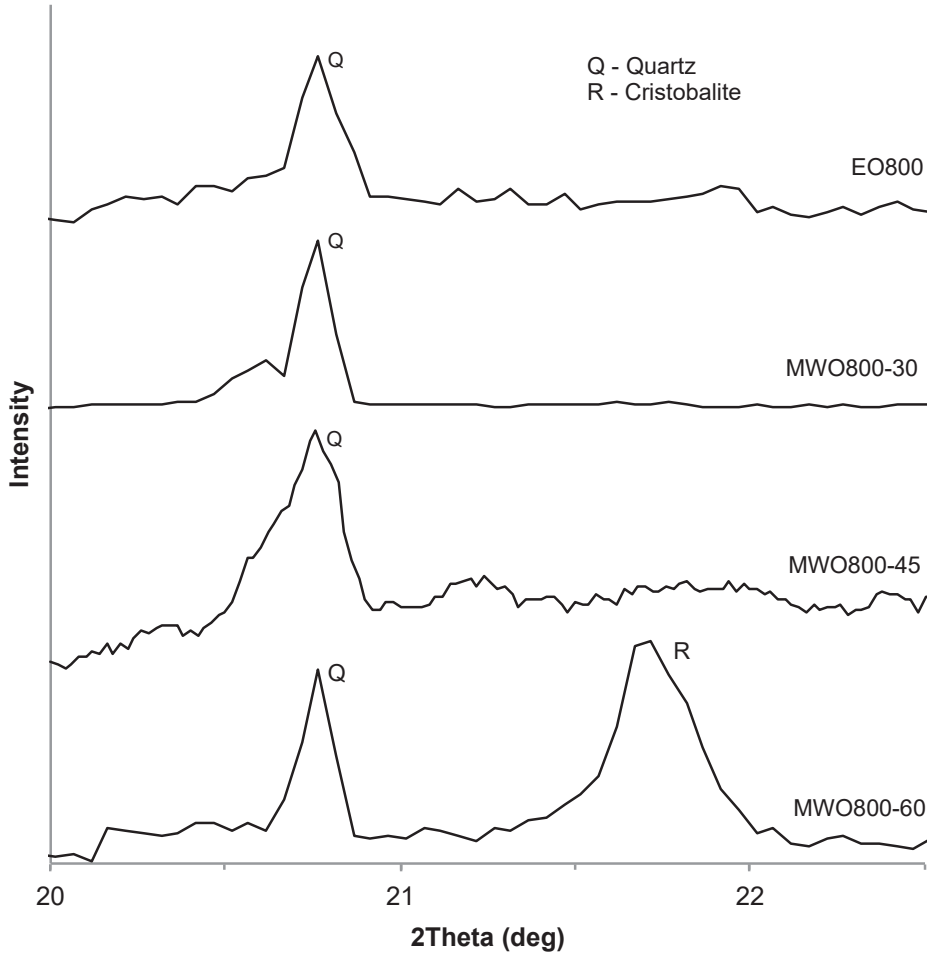



**Fig. 7.** Detailed XRD patterns for SCBA calcined at 800ºC (2Theta 20°–22.5º)

We used the method proposed by Tashima et al. [41] to assess the influence of the calcining conditions on the pozzolanic reactivity of SCBA. The pH and electrical conductivity of CH:SCBA aqueous suspensions of different proportions were monitored for seven days. Tashima et al. [41] represent the electrical conductivity results in terms of a loss of electrical conductivity, LC (%), which is calculated according to Eqs. (1) and (2):

$$LC(\%)_{\mathrm{t}} = \frac{C_0 - C_{\mathrm{t,C}}}{C_0}\, x\, 100 \quad (1)$$

$$C_{\mathrm{t,C}} = C_{\mathrm{t}} - C_{\mathrm{t,poz}} \quad (2)$$

where $C_0$ is the electrical conductivity of a calcium hydroxide suspension before the addition of

pozzolan; $C_t$ is the electrical conductivity measured over t hours; $C_{t,poz}$ is the electrical conductivity of the pozzolan (SCBA) measured over t hours; and $C_{t,C}$ is the corrected electrical conductivity over t hours.

Fig. 8 shows typical conductivity loss curves for the CH:SCBA suspensions. For all the samples analysed here, the conductivity loss increased throughout the first four hours as SCBA is added to the suspension, due to adsorption of the dissolved $Ca^{+2}$/$OH^-$ ions onto SCBA particles.

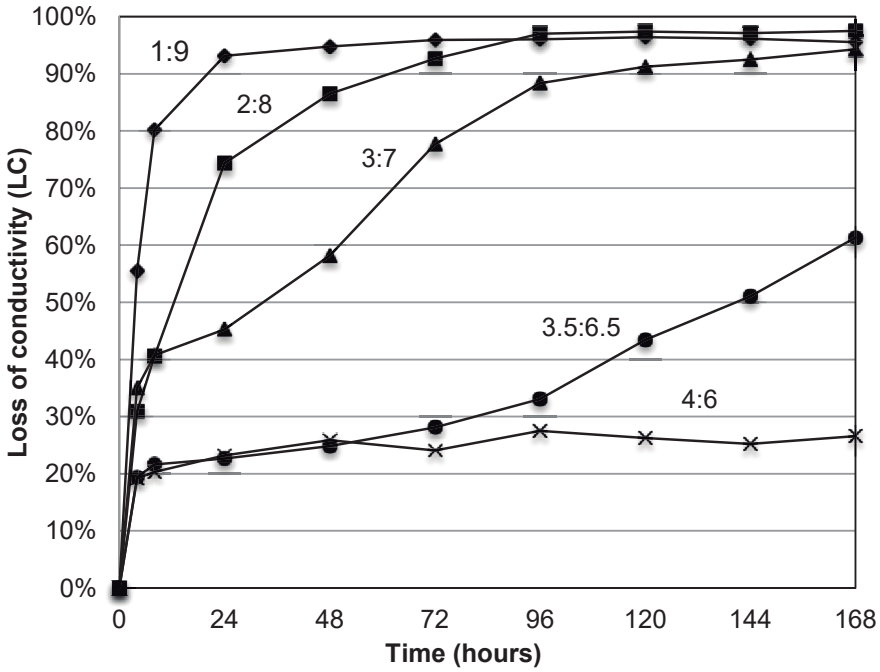



**Fig. 8.** LC(%) for CH:SCBA (MWO600-30) suspensions tested over seven days at 60°C

After the fourth hour, the curves take one of two forms. In the first case, the mixture remains in the saturated state, and the LC(%) value is constant throughout the test period of 4–168 h, while in the second, there is an increase in the LC(%) value throughout the test period, since the suspension reaches an unsaturated state. This unsaturation is due to the consumption of the solid phase of CH via the pozzolanic reaction. The final LC(%) value and the time taken to reach this unsaturated state depend on the CH:pozzolan ratio and the pozzolanic reactivity. For

example, Figure 8 shows that mixtures with ratios 1:9, 2:8 and 3:7 reached an unsaturated state within the first eight hours of the reaction, while the 3.5:6.5 mixture reached unsaturation after 96 hours.

Fig. 9 shows the pH values of the CH suspensions, measured before the addition of SCBA and over the seven days of the test. In the same way as the LC(%) assessment, two types of curves are observed. In the first case, the pH value is constant throughout the test, as the mixture remains saturated with CH; in the second, unsaturation occurs and the pH value drops (i.e. the $OH^-$ concentration decreases) due to the fixation of hydroxide anions in the pozzolanic reaction.

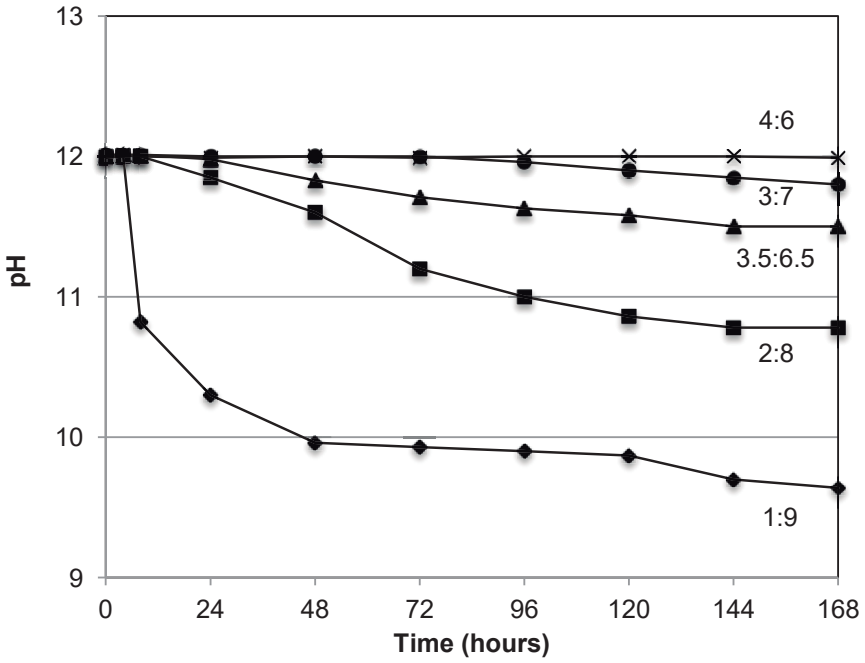



**Fig. 9.** pH values of CH:SCBA (MWO600-30) suspensions tested over seven days at 60°C

Using the method proposed by Tashima et al. [41], unsaturation occurred when LC(%) was higher than 30% relative to the saturated CH suspension, and also when the decrease in pH (ΔpH) was greater than 0.15 units. Table 3 presents the results of LC(%) and ΔpH for the suspensions at 60°C. We analysed suspensions with CH:SCBA ratios of 1:9, 2:8, 3:7, 3.5:6.5 and

4:6, using the SCBA after various calcination treatments.

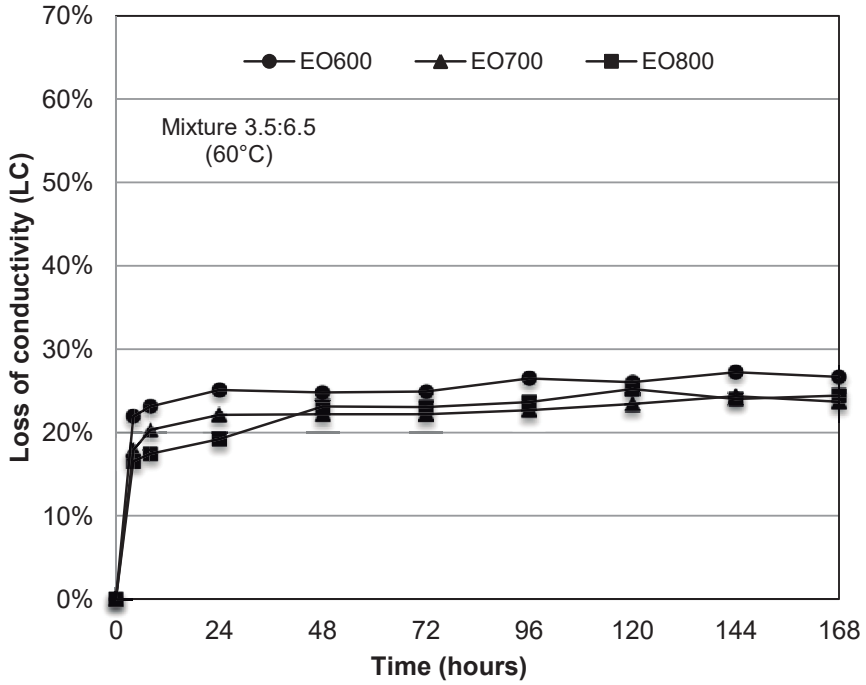
**Table 3.** ΔpH and LC(%) values for CH:SCBA suspensions at 60°C, tested over seven days

| Mixtures (CH:SCBA) 60°C | | Electric oven | | | Microwave oven | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | 600°C | | | 700°C | | | 800°C | | |
| | | 600°C | 700°C | 800°C | 30 min | 45 min | 60 min | 30 min | 45 min | 60 min | 30 min | 45 min | 60 min |
| 1:9 | LC(%) | **97** | **89** | **90** | **95** | **97** | **97** | **98** | **94** | **95** | **96** | **95** | **93** |
| | ΔpH | **2.36** | **1.81** | **1.6** | **1.63** | **1.73** | **1.76** | **1.78** | **1.58** | **1.71** | **1.26** | **1.13** | **1.09** |
| 2:8 | LC(%) | **93** | **88** | **82** | **98** | **96** | **95** | **91** | **94** | **83** | **89** | **90** | **85** |
| | ΔpH | **1.21** | **1.06** | **0.89** | **1.02** | **1.01** | **0.99** | **0.75** | **0.99** | **0.72** | **0.7** | **0.54** | **0.48** |
| 3:7 | LC(%) | **72** | **68** | **48** | **94** | **84** | **64** | **70** | **71** | **59** | **73** | **59** | **38** |
| | ΔpH | **0.51** | **0.42** | **0.32** | **0.43** | **0.3** | **0.29** | **0.39** | **0.23** | **0.15** | **0.18** | **0.16** | **0.15** |
| 3.5:6.5 | LC(%) | 27 | 24 | 24 | **61** | **52** | 25 | **32** | 26 | 25 | 25 | 27 | 27 |
| | ΔpH | 0.02 | 0.01 | 0.05 | **0.2** | **0.18** | 0.03 | **0.18** | 0.00 | 0.01 | 0.02 | 0.00 | 0.01 |
| 4:6 | LC(%) | 27 | 26 | 23 | 27 | 26 | 26 | 25 | 26 | 23 | 24 | 24 | 23 |
| | ΔpH | 0.01 | 0,00 | 0.02 | 0.01 | 0.00 | 0.00 | 0.00 | 0.02 | 0.00 | 0,01 | 0.00 | 0.02 |

* Bold numbers represent LC(%) > 0.3 or ΔpH > 0.15

The results in Table 3 show that the suspensions with the highest SCBA contents (1:9 and 2:8) performed similarly for all SCBA calcination treatments, reaching unsaturation in the first few hours of the test and showing LC(%) values of approximately 90% at the end of the test. The suspension with the lowest SCBA content (4:6) showed constant LC(%) values of approximately 25% for the first four hours of the test, indicating that unsaturation had not been reached. It was not possible to determine the influence of the calcining process on the SCBA reactivity of these suspensions (1:9, 2:8 and 4:6) in this analysis.

However, it is possible to observe several differences in the performance of the SCBA as a function of the calcination treatment used, in suspensions with intermediate levels of SCBA (3:7 and 3.5:6.5). Particularly for the 3.5:6.5 suspension (Figure 10), the SCBA subjected to the MWO600-30, MWO600-45 and MWO700-30 calcining treatments showed a greater capacity for CH consumption, indicating a higher pozzolanic reactivity.

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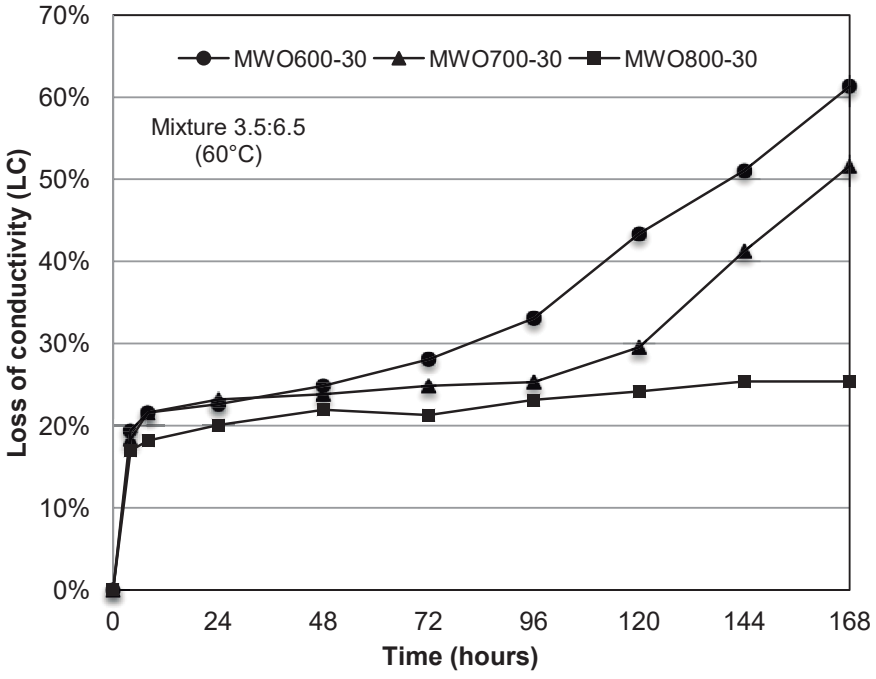
288 (a)

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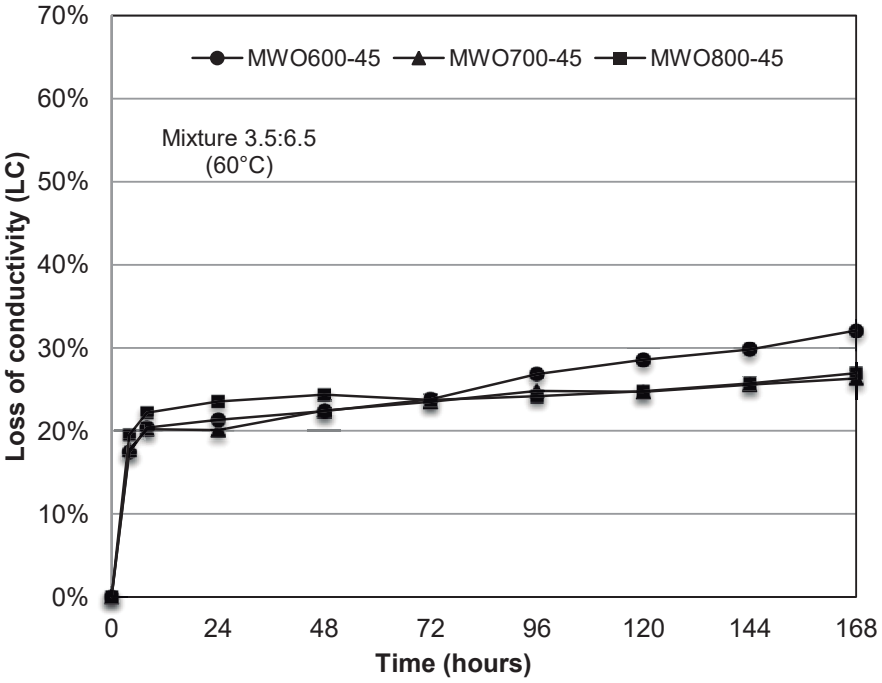
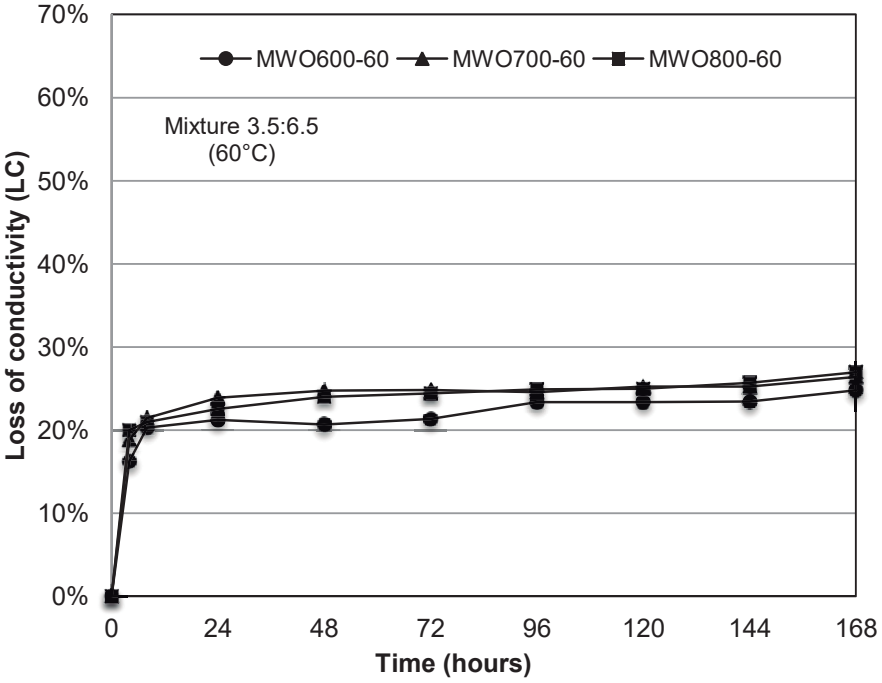
290 (b)




(c)




(d)

**Fig. 10.** LC(%) for 3.5:6.5 (CH:SCBA) mixture tested for seven days at 60°C: (a) in an electric oven; (b) in a

296 microwave oven for 30 minutes; (c) in a microwave oven for 45 minutes; and (d) in a microwave oven for 60
297 minutes
298
299 Based on these results, several CH:SCBA suspensions calcined at 40°C and 50°C were also
300 evaluated using the method proposed by Tashima et al. [41]; this allowed us to determine
301 whether the behaviour observed at 60°C was repeated at lower temperatures, since a reduction
302 in temperature slows the pozzolanic reaction rate, decreasing the LC(%) values during the tests.
303 The behaviour of the calcining treatments with the best performance, i.e. at 60°C (MWO600-30
304 and MWO700-30), was compared to the corresponding electric oven treatments (EO600 and
305 EO700). Aqueous suspensions with CH:SCBA ratios of 1:9, 2:8, 2.5:7.5, 3:7, 3.5:6.5 and 4:6 were
306 analysed.
307 Tables 4 and 5 show the results of ΔpH and LC(%) for the suspensions analysed at 40°C and
308 50°C, respectively. These results confirm those obtained at 60°C, and show that microwave
309 calcination for 30 minutes results in more reactive ash than calcination in an electric oven for one
310 hour. The results obtained for the 3:7 suspension at 40°C indicate that only the ashes that
311 underwent microwave calcination at 600°C for 30 minutes (MWO600-30) reached unsaturation at
312 the end of the test.
313
314 **Table 4.** ΔpH values and LC(%) for suspensions tested at 50°C

| **Mixtures** (CH:SCBA) 50°C | | **Electric oven** | | **Microwave oven** (30 min) | |
|---|---|---|---|---|---|
| | | 600°C | 700°C | 600°C | 700°C |
| 1:9 | LC(%) | **93** | **95** | **93** | **95** |
| | ΔpH | **1.5** | **1.15** | **1.67** | **1.5** |
| 2:8 | LC(%) | **92** | **93** | **93** | **93** |
| | ΔpH | **0.86** | **0.6** | **1.2** | **0.84** |
| 2.5:7.5 | LC(%) | **85** | **83** | **92** | **83** |
| | ΔpH | **0.56** | **0.46** | **0.56** | **0.54** |
| 3:7 | LC(%) | **61** | **55** | **83** | **73** |
| | ΔpH | **0.21** | **0.2** | **0.43** | **0.27** |

| | | | | | |
|---|---|---|---|---|---|
| 3.5:6.5 | LC(%) | 26 | 27 | **43** | **40** |
| | ΔpH | 0.00 | 0.01 | **0.16** | **0.18** |
| 4:6 | LC(%) | 23 | 28 | 28 | 27 |
| | ΔpH | 0.01 | 0.00 | 0.01 | 0.01 |

315

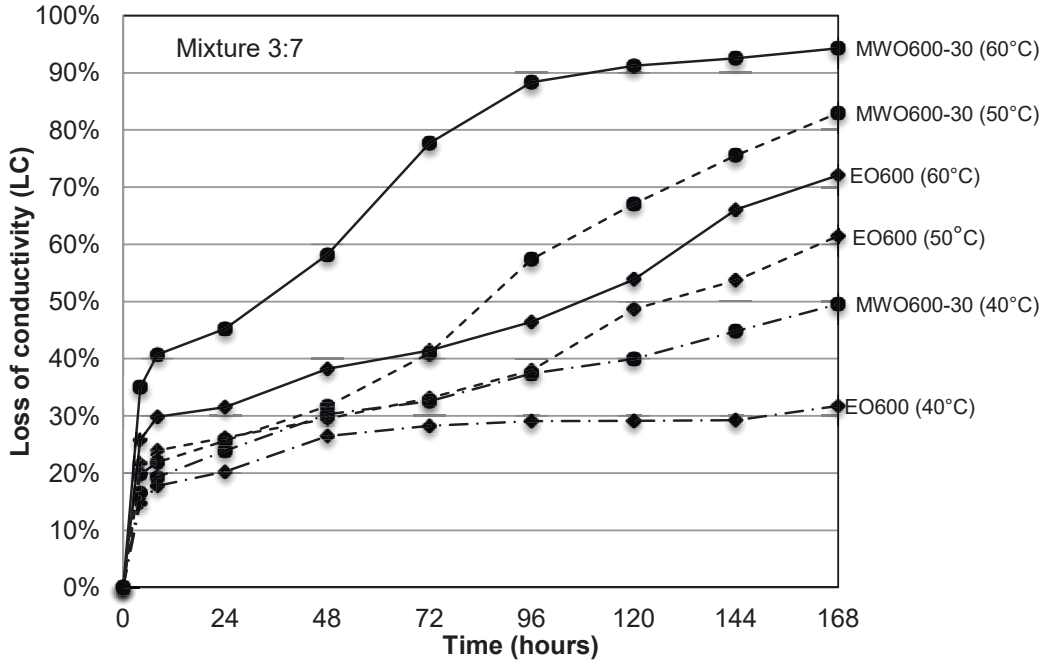
316 **Table 5.** ΔpH values and LC(%) for suspensions tested at 40°C

| **Mixtures** (CH:SCBA) 40°C | | **Electric oven** | | **Microwave oven** (30 min) | |
|---|---|---|---|---|---|
| | | 600°C | 700°C | 600°C | 700°C |
| 1:9 | LC(%) | **92** | **86** | **88** | **86** |
| | ΔpH | **1.3** | **1.43** | **1.72** | **1.37** |
| 2:8 | LC(%) | **88** | **71** | **84** | **80** |
| | ΔpH | **0.84** | **0.36** | **0.93** | **0.66** |
| 2.5:7.5 | LC(%) | **54** | **50** | **73** | **80** |
| | ΔpH | **0.24** | **0.15** | **0.43** | **0.49** |
| 3:7 | LC(%) | 28 | 27 | **50** | **32** |
| | ΔpH | 0.10 | 0.13 | **0.19** | 0.06 |
| 3.5:6.5 | LC(%) | 26 | 24 | 28 | 27 |
| | ΔpH | 0.03 | 0.02 | 0.01 | 0.02 |
| 4:6 | LC(%) | 25 | 25 | 25 | 27 |
| | ΔpH | 0.02 | 0.01 | 0.01 | 0.03 |

317

318 After evaluating the pozzolanic reactivity using the method proposed by Tashima et al. [41],
319 the results showed that both types of treatment yielded materials with a medium level of
320 pozzolanic reactivity. However, a comparison of these results shows that the use of the
321 microwave oven for SCBA calcination results in a more reactive ash with a lower calcination time
322 than the electric oven. This is confirmed by an analysis of the reactivity of the 3:7 suspension at
323 temperatures of 40°C, 50°C and 60°C for the ashes undergoing treatments EO600 and
324 MWO600-30 (Figure 11). For all temperatures examined, the reactivity of the ash calcined in the
325 microwave oven (MWO600-30) was higher than that calcined in the electric oven (EO600), within
326 the first 24 hours of analysis.

327




328

329 **Fig. 11.** LC(%) for mixture 3:7 (CH:SCBA) tested over seven days at 40°C, 50°C and 60°C, for ashes
330 undergoing treatments EO600 and MWO600-30

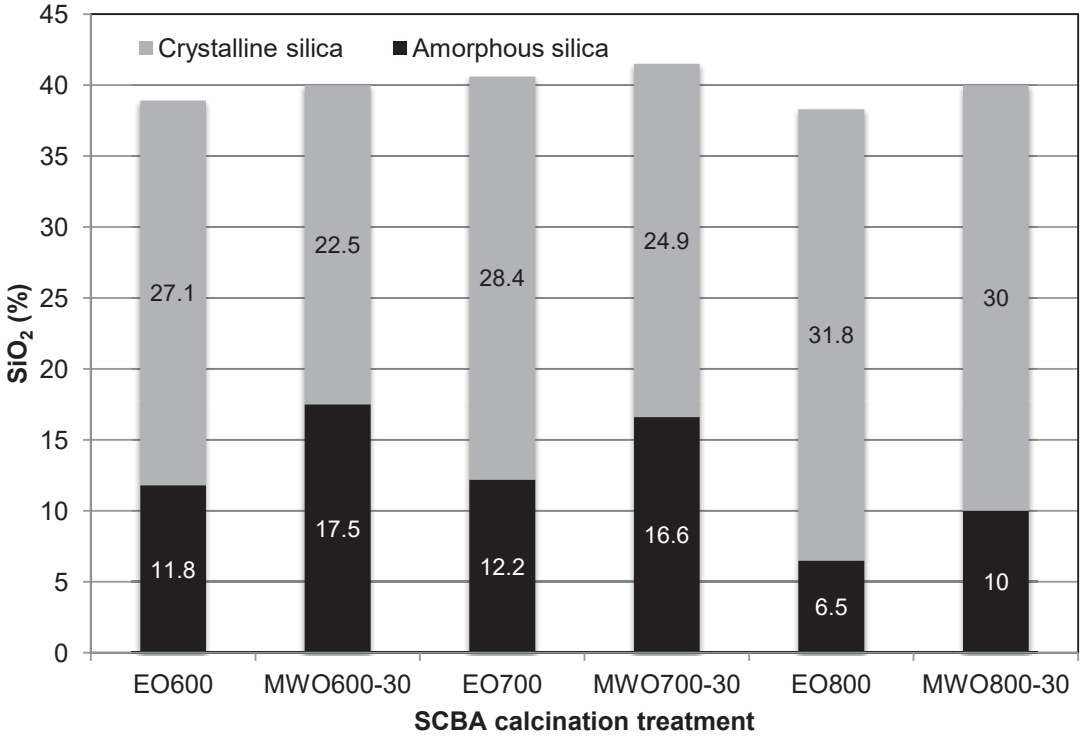
331

332 In order to understand the potential pozzolanic reactivity in mixtures of pozzolans with Portland
333 cement, it is necessary to know the content of amorphous and crystalline silica. In general, the
334 pozzolanic reactivity of SCBA is directly related to the content of silica in the amorphous state [14,
335 17-20, 46-47]. The procedures in UNE 80225:1993 [43] and UNE-EN 196-2:1996 [44] were used
336 to evaluate the influence of the calcining treatment on the amorphous silica content of SCBA,
337 although the time of extractive treatment with 4M KOH was reduced from 4 hours to 3 minutes, as
338 described by Payá et al. [45].

339 An analysis was carried out of the amorphous silica content of ashes undergoing microwave
340 calcination for 30 minutes in an electric oven for one hour at temperatures of 600ºC, 700ºC and
341 800ºC.

342 Fig. 12 shows that the total amount of silica present in the ashes ranged from 38.5% to 41.5%.
343 These data slightly differ from those obtained by XRF (Table 1), which were between 37.5% and

344 39.5%, although it should be noted that these methods are very different.




345

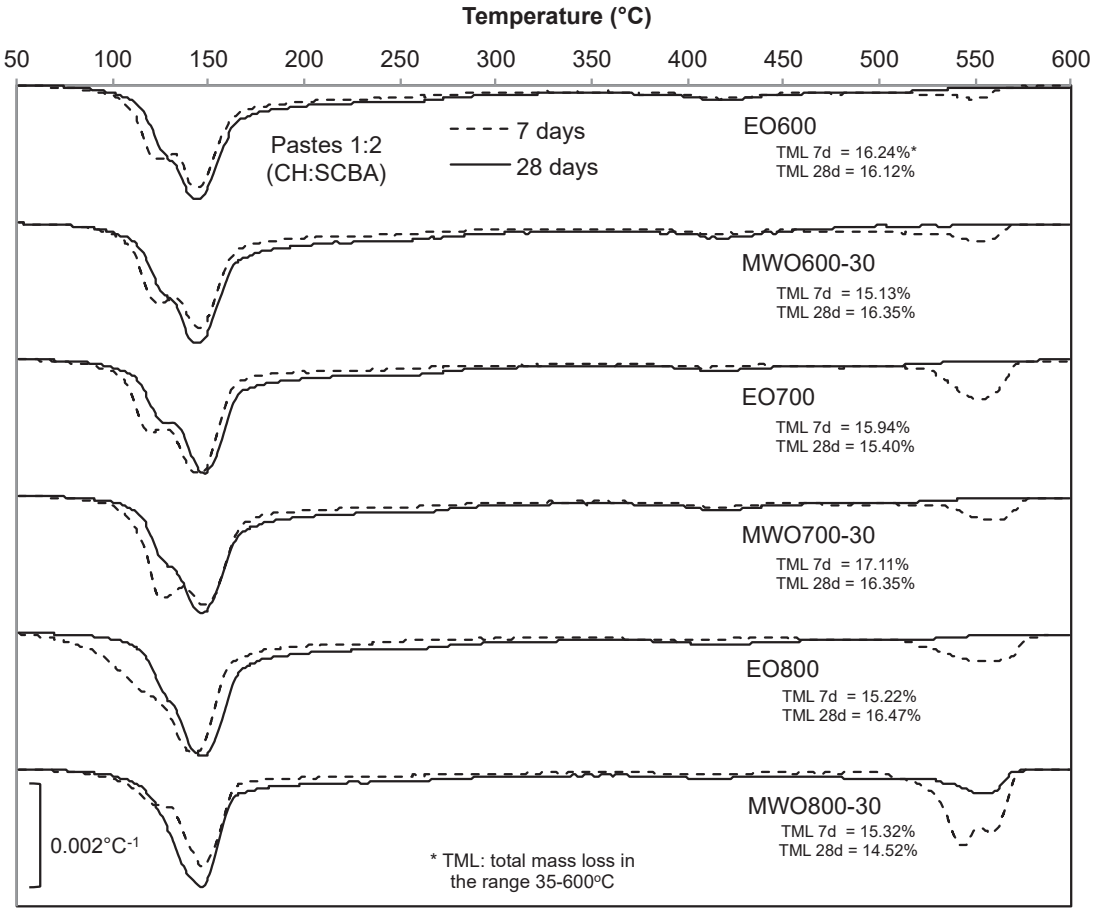
346 **Fig. 12.** Silica (amorphous and crystalline) content of SCBA samples

347

348 Calcination in a microwave oven for 30 minutes at temperatures of 600°C and 700°C resulted
349 in ashes with the highest amorphous silica content (17.5% and 16.6% respectively). For
350 MWO600-30 and MWO700-30, there was an increase of about 50% and 35% in amorphous silica
351 compared to EO600 and EO700, respectively. These results are in accordance with those
352 obtained in the pozzolanic reactivity tests, showing that the SCBA undergoing MWO600-30
353 treatment gave the most reactive ash of the treatments studied.

354 Figures 13 and 14 show derivative thermogravimetric (DTG) curves from TGA for the 1:2 and
355 1:1 CH:SCBA pastes, respectively. Ashes undergoing calcination at 600ºC, 700ºC and 800ºC in a
356 microwave oven for 30 minutes and in an electric oven for one hour were used in an assessment
357 of the reactivity. The DTG curves showed two main zones; the dehydration of compounds formed
358 through the pozzolanic reaction, and especially the C-S-H gel, occurred mainly within a

359 temperature range of 100°C–180°C, while mass loss by CH dehydration occurred within a
360 temperature range of 520°C–570°C.



361

362 **Fig. 13.** DTG curves for CH:SCBA pastes (1:2) cured for seven and 28 days

363

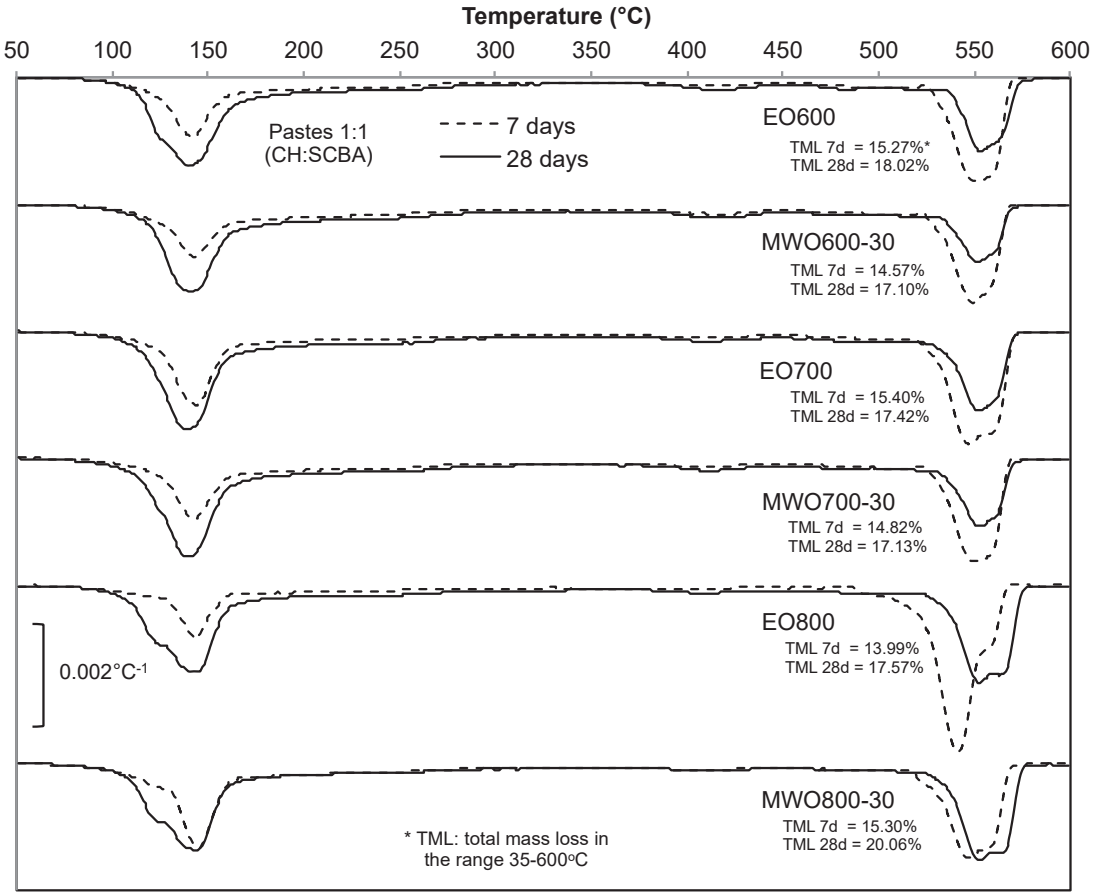



**Fig. 14.** DTG curves for CH:SCBA pastes (1:1) cured for seven and 28 days

Figure 13 (1:2 CH:SCBA pastes) shows that the difference in the total mass loss (TML) between seven and 28 days, is small. This can be attributed to the use of CH as the limiting reagent. Figure 14 (1:1 CH:SCBA pastes) shows that there is an increase in the mass loss with an increase in curing time (from seven to 28 days); this is related to the compounds formed by the pozzolanic reaction, as the SCBA continues to react with CH, forming C-S-H, which increases the amount of water released in the heating process. In this case, CH is not the limiting reagent for the pozzolanic reaction.

An analysis of the 1:2 pastes (Fig. 13) shows that at 28 days, CH was almost completely consumed in the pozzolanic reaction, although the MWO800-30 sample contained a small

quantity of unreacted CH. This behaviour confirms the good pozzolanic properties of the tested ashes. In the 1:1 pastes (Fig. 14), CH consumption was not complete at 28 days, and the influence of the calcination treatment on the ability of SCBA to react with CH can be observed in more detail.

Based on the mass loss due to dehydration of CH ($Ca(OH)_2$) from the pastes in a temperature range 520°C–570°C, the amount of lime fixed by the pozzolanic reaction can be quantified. This is defined in Eq. (3), where $(CH)_0$ and $(CH)_{SCBA}$ are the initial and final amounts of CH in the CH:SCBA paste [48], respectively:

$$\text{Fixed } \mathrm{Ca(OH)_2}(\%) = \frac{(CH)_0 - (CH)_{SCBA}}{(CH)_0} \text{x } 100 \quad (3)$$

An evaluation of the CH fixation (Figures 15 and 16) indicates that all of the calcination treatments resulted in SCBA with lime fixation capacity, due to the formation of C-S-H in the pastes. However, of all the calcination treatments analysed, MWO600-30 resulted in an ash with the highest lime fixation capacity (80%), indicating greater pozzolanic reactivity.

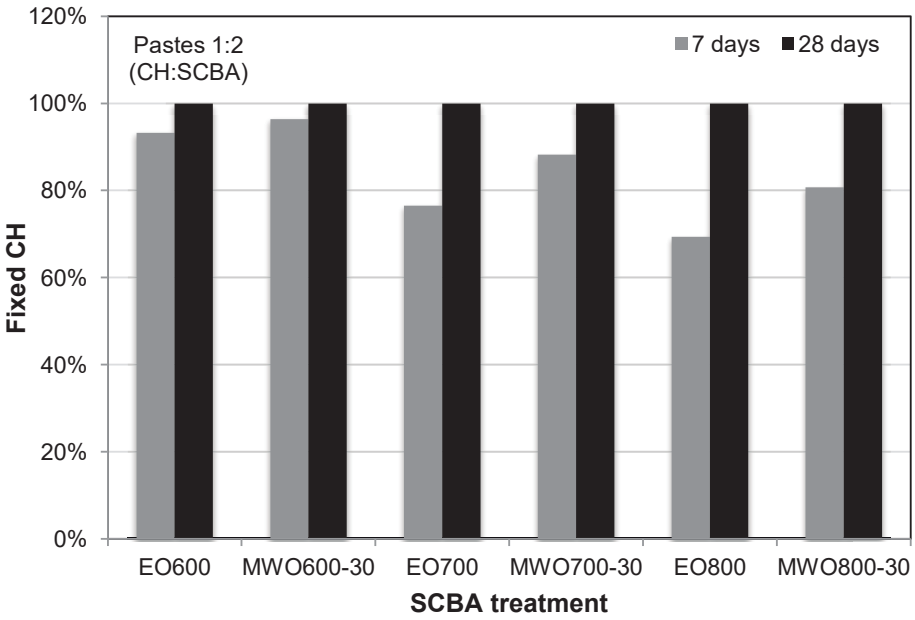



**Fig. 15.** Lime fixed by CH:SCBA pastes (1:2) cured for seven and 28 days

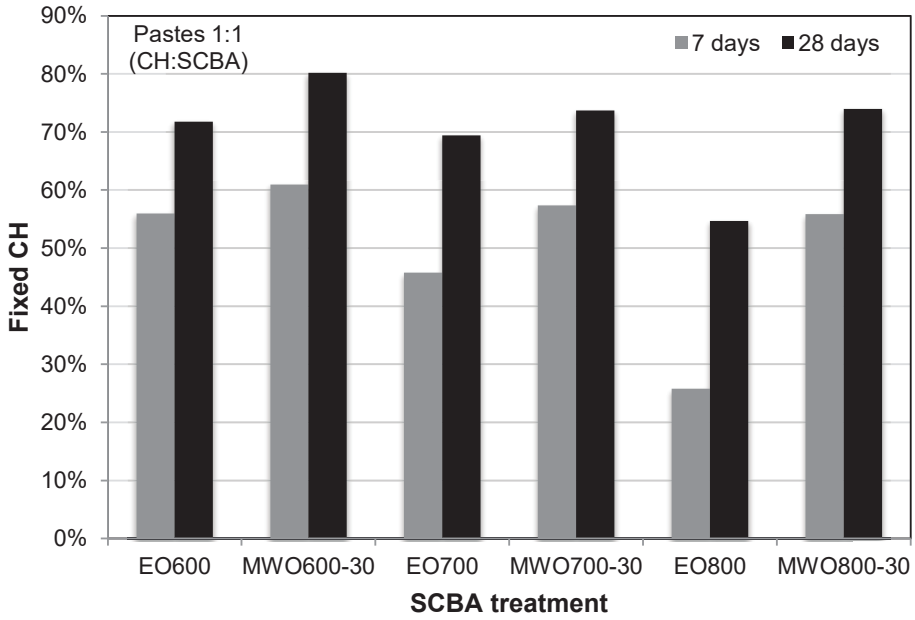



**Fig. 16.** Lime fixed for CH:SCBA pastes (1:1) cured for seven and 28 days

The results of this study indicate that the use of a microwave oven for SCBA calcination requires shorter burning times and results in ashes with greater pozzolanic reactivity, allowing for considerable energy savings. This is probably due to the higher calcining efficiency of SCBA in microwaves [23, 24, 35], particularly due to the high carbon content of SCBA [30-34].

## 4. Conclusions

This study compares the performance of SCBA calcined in a microwave oven and electric oven. Based on the results obtained, the following conclusions can be drawn:

- Calcining treatments of SCBA give greater homogenisation of the material, since they considerably reduce the amount of organic/carbonaceous material.
- In terms of reducing LOI values, calcination in a microwave oven was more efficient than in an electric oven.

- An analysis of amorphous silica indicated that calcination in a microwave oven for 30 min at 600°C gave SCBA with the highest amorphous silica content of all the treatments considered here.
- SCBA calcined in a microwave oven for 30 min at 600°C also showed the best performance in terms of pozzolanic reactivity, and pH and electrical conductivity and fixed lime in CH pastes confirmed this trend.
- We therefore conclude that the use of a microwave oven gives SCBA with greater pozzolanic reactivity. The calcining process is also significantly more efficient than in an electric oven, since this allows a 50% reduction in the calcining time and the use of a temperature of 600°C, lower than that usually applied.

**Acknowledgements**

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