

Hydration and strength evolution of air-cured zeolite-rich tuffs and siltstone blended cement pastes at low water-to-binder ratio

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ABSTRACT: This contribution is the second part of an in-depth study on the hydration and strength evolution of blended cement pastes at a water to binder (W/B) ratio of 0.3, cured by two different methods. The blended cement pastes showed significant hydration up to 7 days, when almost all of the hydration products had already formed; thereafter, carbonation played an important role up to, and possibly beyond, 91 days. Likewise, the hydration of alite (tricalcium silicate, Ca_3SiO_5 , C3S) proceeded up to 14 days and then started to slow down. However, the hydration of belite (dicalcium silicate, Ca_2SiO_4 , C2S) was affected most strongly, as it nearly ceased, under the air-curing conditions. During hydration, some of the blended cement pastes had a larger calcium hydroxide (CH) content than the unblended (plain) ones. The accelerating effects of the addition of supplementary cementitious materials (SCMs), the air-curing conditions and the low W/B ratio may explain these unusual results. Under these experimental conditions, the water incorporated into hydrates was about 50% of the total amount of water used during full hydration of the cement pastes. The pozzolanic reaction predominated during the early ages, but disappeared as time passed. In contrast, the carbonation reaction increased by consuming ~45% of the total amount of CH produced after aging for 91 days. Only one blended cement paste reached the compressive strength of the plain cements. The blended cement pastes containing 5% of the zeolitic tuffs, Zeo1 or Zeo2, or 10% of the calcareous siltstone, Limo, developed the greatest compressive strength under the experimental conditions used in this study.

KEYWORDS: pozzolanic reaction, natural zeolites, air curing, quantitative X-ray diffraction.

The incorporation of supplementary cementitious materials (SCMs) during cement hydration is very important as it has a favourable effect on the durability and mechanical performance of the cement. Additions of zeolitic material, in particular, have proven beneficial to the durability and

compressive strength of cement-based materials (Ahmadi & Shekarchi, 2010; Snellings *et al.*, 2012; Valipour *et al.*, 2013). However, the impact of the SCMs does not depend only on the intrinsic properties of the zeolitic tuffs, such as cation exchange capacity (CEC), type of exchangeable cation, fine particle size and content of the reactive phases, but also on external factors like the mix design, the curing conditions and the water to binder ratio (W/B) (Colella *et al.*, 2001; Siddique &

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Klaus, 2009; Scrivener & Nonat, 2011; Snellings *et al.*, 2012).

A proper combination of mineral addition and low W/B ratios produces high-performance concrete that is normally cured in air. Although these parameters have been investigated thoroughly in the past (Sabir and Wild, 2001; Mertens *et al.*, 2009; Siddque & Klaus, 2009; Snellings *et al.*, 2012; Estoková & Kovalčíková, 2013), there are several issues that still need to be resolved.

The effects of the amount of mineral replacement, W/B ratio and curing conditions on the hydration process have been studied extensively. The mineral addition affects the hydration process according to the proportion of the mineral used. Low-level replacement by SCM increases the proportion of hydrates in blended cement pastes (Kontori *et al.*, 2009; Lilkov *et al.*, 2011a) while increasing the rate of hydration (Ogawa *et al.*, 1980; Snellings *et al.*, 2010), but this also increases the water demand (Yilmaz & Ediz, 2008; Lilkov *et al.*, 2011b; Kocak *et al.*, 2013) and the required carbonation (Cultrone *et al.*, 2005; Khunthongkeaw *et al.*, 2011; Vigil de la Villa *et al.*, 2013). In the case of extensive replacement of SCMs, water demand and carbonation are increased further by self-neutralization (Hanchara *et al.*, 2001; Lothenbach *et al.*, 2011) and self-desiccation (Gleize and Cyr, 2007; Meddah, 2009).

The influence of the amount of mineral addition depends also on the W/B ratio as it affects the moisture content directly during the early hydration process (Meeks & Carino, 1999). At high W/B ratios, complete hydration and improvement in the pozzolanic reaction are expected (Poon *et al.*, 1999; Brouwers, 2004, 2005; Sata *et al.*, 2012). In addition to changes in volume, porosity changes and strength gain have been observed (Al-Amoudi *et al.*, 2009; Sata *et al.*, 2012; Zeng *et al.*, 2012). At low W/B ratios, the hydration process of blended cement pastes is far from complete, due to the limited abundance of water; thus un-hydrated cement phases can be observed even after aging for 91 days (Cornejo *et al.*, 2014). In addition, self-desiccation and autogenous shrinkage are also expected to affect the final performance of cement-based materials (Loukili *et al.*, 1999; Meeks & Carino, 1999).

From a purely practical point of view, air-conditioning is the long-term curing procedure for almost all civil infrastructures. The air-curing conditions normally increase carbonation (Pacheco *et al.*, 2012) and cause incomplete hydration

(Safiuddin *et al.*, 2007), self-neutralization (Hanchara *et al.*, 2001) and drying shrinkage (Poon *et al.*, 1997). These effects are most probably caused by decreasing the capacity for retaining sufficient water during the hydration and pozzolanic reactions (Miller & Sakulich, 2011). As the air-curing conditions are more important for long-term reactions than for short-term ones, the C2S phase, which usually reacts after 21 days, is the most readily affected cement phase (Termkhajornkit & Nawa, 2006). On the other hand, the influence of air-curing conditions is greater at low, rather than at high, W/B ratios. For W/B ratios >0.5, air-curing conditions are most important when there is high replacement with SCMs (Ramezaniapour, 1995; Ozer & Ozkul, 2004; Sajedi *et al.*, 2012). However, for W/B ratios of <0.4, air curing becomes more effective at low SCM content rather than high (Bentz *et al.*, 1997).

Although, in general, there is a lack of correlation between the degree of hydration and compressive strength (Escalante-Garcia & Sharp, 1998; Scrivener & Nonat, 2011), there are some overall trends that can be highlighted. The effect of SCMs over compressive strength is greater at low water contents than at high contents (Poon *et al.*, 1999; Najimi *et al.*, 2012). In the case of zeolitic-tuffs used as SCMs, the optimal compressive strength is achieved within the range of 10–20% addition (Canpolat *et al.*, 2004; Ahmadi & Shekarchi, 2010; Valipour *et al.*, 2013).

In spite of the large number of studies on the effects of SCMs on hydration, there are few reported studies of the hydration processes occurring within blended cement pastes under air-curing conditions, at a low W/B ratio of 0.3 without chemical additives. This study compared two zeolitic tuffs and one calcareous siltstone currently used in the manufacture of Portland cement and aims to investigate: (1) the effect of the SCM on the hydration and compressive strength at low W/B ratio using air-curing conditions; and (2) to determine the optimum dosage of SCM to achieve maximum mechanical performance under these conditions.

EXPERIMENTAL

Materials

Blended cement pastes composed of Ordinary Portland cement (OPC), mineral additives and tap

water, were used to evaluate the hydration process and strength evolution under air-curing conditions. The mineral additives used were two zeolite-rich tuffs coded as Zeo1, Zeo2 and one calcareous siltstone coded as Limo. Samples Zeo1 and Limo were collected close to Guayaquil, Ecuador and Zeo2, from the Pacific coastal region of Ecuador. The UTM coordinates for the location of Zeo1 are 17S/591661/9776846, for Zeo2 are 17S/528476/9815842 and for Limo are 17S/608547/9760423.

The mineralogical characterization and chemical analyses of these SCMs were reported by Cornejo *et al.* (2014). Briefly, Zeo1 is a high-purity mordenite (MOR) tuff (average 73% mordenite), with minor quantities of quartz (Qz) and clay minerals. The Zeo2 sample is composed of a mixture of heulandite-clinoptilolite (Hul-Cpt) and mordenite with minor quantities of quartz (Qz) and calcite (Cal), while Limo contains calcite (~27%), quartz, cristobalite and clay minerals. The reactive silica content was 57%, 60% and 47% for the Zeo1, Zeo2 and Limo, respectively. These zeolitic tuffs were reported previously as Ca-clinoptilolite, Ca-heulandite and Na-Ca-mordenite (Machiels, 2010; Machiels *et al.*, 2008, 2014).

The physical and chemical characteristics of the OPC used in this study, were described by Cornejo *et al.* (2014). In summary, the physical and chemical characteristics of this OPC followed the Ecuadorian standard, INEN 152:2012. The pozzolanic activity was evaluated with the Frattini test (EN-196-5:2005) described by Cornejo *et al.* (2014). Only Zeo2 fixed an adequate amount of lime after 7 days to be considered as a pozzolanic material. At 15 days, all SCMs showed a greater fixation of lime and so all were consequently considered as pozzolanic materials.

Sample preparation

After removing organic matter, the collected samples were crushed with a hammer, then with a jaw crusher and finally ground with a ball mill so that 70 wt.% of the materials were finer than 375 mesh. Subsequently, the components of the blended cement pastes were mixed using tap water at a W/B ratio of 0.3, using vibration to remove bubbles. The specimens were moulded quickly inside 50-mm cube moulds to avoid loss of material and undesired setting and covered with paraffin films to avoid further evaporation. Finally, each specimen was brought to a curing site in the laboratory at

25.6±1.6°C and 68.8±3.9% relative humidity in controlled indoor conditions and allowed to cure for a predetermined time, after which they were broken (ASTM C109:2013). Selected broken samples were stored in ethanol to prevent hydration.

The evolution of hardening and hydration was evaluated with uni-axial compressive strength tests, quantitative X-ray diffraction (XRD), thermogravimetric analysis-differential scanning calorimetry (TGA-DSC), scanning electron microscopy with energy dispersive spectroscopy (SEM-EDS) and density measurements.

Experimental settings: calibration and replication

Calibration and replication were used for comparison and complementary analysis. A randomized block with one blocking factor was used for the two analyses. Without repeating the same combination of factors and levels, these settings allowed the estimation of the effect of mineral addition over a wide range of experimental conditions, increasing confidence in the results, as the analysis of additional data is possible under the same experimental conditions.

As the experimental setting was designed to show equally-separated levels and the experimental factor was proportionate, each proportion level was selected by adding 5% SCM. Therefore, calibration was performed using 0 (control sample with 0% mineral addition), 5, 10, 15, 20 and 25 wt.% mineral addition and replication with 7.5, 12.5, 17.5, 22.5 and 27.5 wt.% mineral addition. The aging times were selected as follows: 7, 14, 21, 28 and 91 days for calibration and 4, 11, 18, 25 and 91 days for replication. The mix design of the blended cement pastes are summarized in Table 1.

Compressive strength

The mechanical performance of the samples were tested in triplicate using a Shimadzu® universal testing machine of 600 KN with an accuracy of 0.5%, allowing calculation of the mean values and the standard deviations, according to ASTM C109:2013.

Analytical techniques

Quantitative X-ray diffraction analysis (XRD). X-ray diffraction analysis was performed using a PANanalytical® X'pert XRD equipped with an

TABLE 1. Mix design for blended cement pastes used at a W/B ratio = 0.3 under air-curing conditions, according to ASTM C109.

	Proportion (%)	Zeolites (g)	Cement (g)	Water (g)
Control	0	0	3000	900
Calibration	5	150	2850	900
	10	300	2700	900
	15	450	2550	900
	20	600	2400	900
	25	750	2250	900
Replication	7.5	225	2775	900
	12.5	375	2625	900
	17.5	525	2475	900
	22.5	675	2325	900
	27.5	825	2175	900

X'Celerator[®] multi-position detector to collect the data, at 45 mA, 40 kV and a divergence slit of 0.478°, using CuK α radiation, a step size of 0.017°2 θ and scanning time of 2 s per step for the raw materials and 10.33 s per step for the cement based materials. The *High Score Plus*[®] software was used for identification and quantification of the crystalline phases.

The hydrated phases in cement pastes and raw materials were quantified using the Rietveld refinement methodology, which compares the experimental XRD traces with theoretical calculated patterns from a structural database by means of the least-squares method until the best fit is achieved (Whitfield & Mitchell, 2003; Mitchell & Margeson, 2006). Corundum and zincite were used as internal standards in the blended cement pastes and the raw zeolite tuffs, respectively. The samples for quantitative analysis were kept in ethanol in a hermetically closed bottle for a predetermined time and then they were kept in a desiccator for 5 days. The dried samples were ground quickly by pestle and mortar to avoid further carbonation, sieved through an ASTM sieve N° 325, mixed with 10 wt.% of the respective internal standard and placed in an XRD sample holder for analysis.

The degree of hydration (DOH) for C3S and C2S quantified by XRD was calculated according to equation 1

$$DOH = \left(\frac{OCP - UCP}{OCP} \times 100 \right) \quad (1)$$

where *DOH* is the degree of hydration of C3S or C2S, *UCP* is the amount of un-hydrated cement phase at a given age and *OCP* is the amount of the original cement phase.

Thermal analysis. The weight losses and heat flows as a function of temperature (TGA-DSC) were measured using a TA[®] Thermal Analyser and was evaluated using *Universal Analysis*[®] software. Selected pieces of the samples after mechanical testing with the universal testing-machine, were placed in a desiccator for 5 days, ground with a pestle and mortar and 6 mg aliquots of the ground samples were heated in 90 μ L alumina crucibles from room temperature to 1100°C with a rate of 20°C min⁻¹ under a nitrogen atmosphere at a flow rate of 100mL/min. The results of thermogravimetric analysis were used to quantify the amount of CH, calcite and water in hydrates normalized (WHN) according to similar studies (Kontori et al., 2009; Borges et al., 2010; Cornejo et al., 2014). Estimation of the amount of CH consumed by carbonation and by the pozzolanic reaction followed the example of Cornejo et al. (2014).

Scanning electron microscopy (SEM). For blended cement pastes, SEM-EDS measurements were carried out using an Inspect FEI[®] SEM equipped with an EDS detector at low-vacuum mode. The operating conditions were 30 Pa pressure, 5 kV accelerating voltage, 2 nm spot size for imaging and 6 nm for EDS analysis with a magnification of 5000 \times .

Density. The density of blended cement pastes was based on ASTM C20 using a Metler Toledo[®] Excellence+ high-precision analytical balance

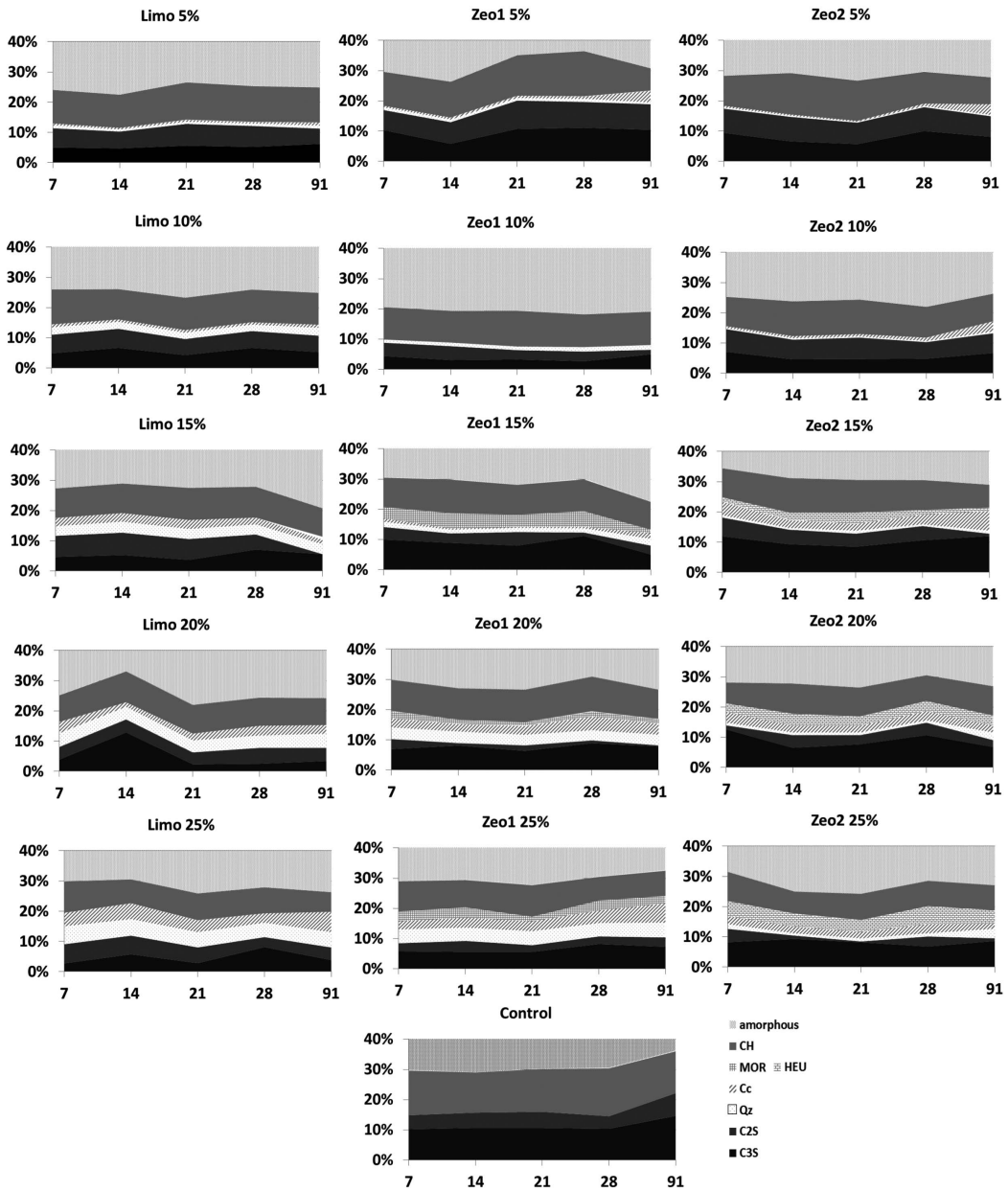


FIG. 1. Plain and blended cement pastes with the same aging time in terms of hydration products and un-hydrated cement phases. The horizontal axis shows the testing times in days.

taking into account corrections for the temperature. The samples were soaked in ethanol, then dried in a desiccator, weighed in air and the weighed, dry samples were placed in a beaker filled with distilled water and the weights were recorded under water after they were stabilized.

RESULTS AND DISCUSSION

Effect of SCMs on hydration products

The blended cement pastes, cured in air with a W/B ratio of 0.3, formed hydration products almost exclusively, up to 7 days, after which carbonation

played an important role during hydration. The hydration products, the un-hydrated cement phases and the amorphous content (considered as a C-S-H phase (Matsushita and Hoshino, 2007)) of the plain and blended cement pastes are shown in Fig. 1. The CH and C-S-H content were affected strongly by air

curing, which slowly stopped the hydration. It was estimated that ~97% of the total amount of CH and 98% of the total amount of C-S-H were already formed before 7 days were complete. The amounts of the C3S and C2S phases remained almost constant during early hydration then appeared to

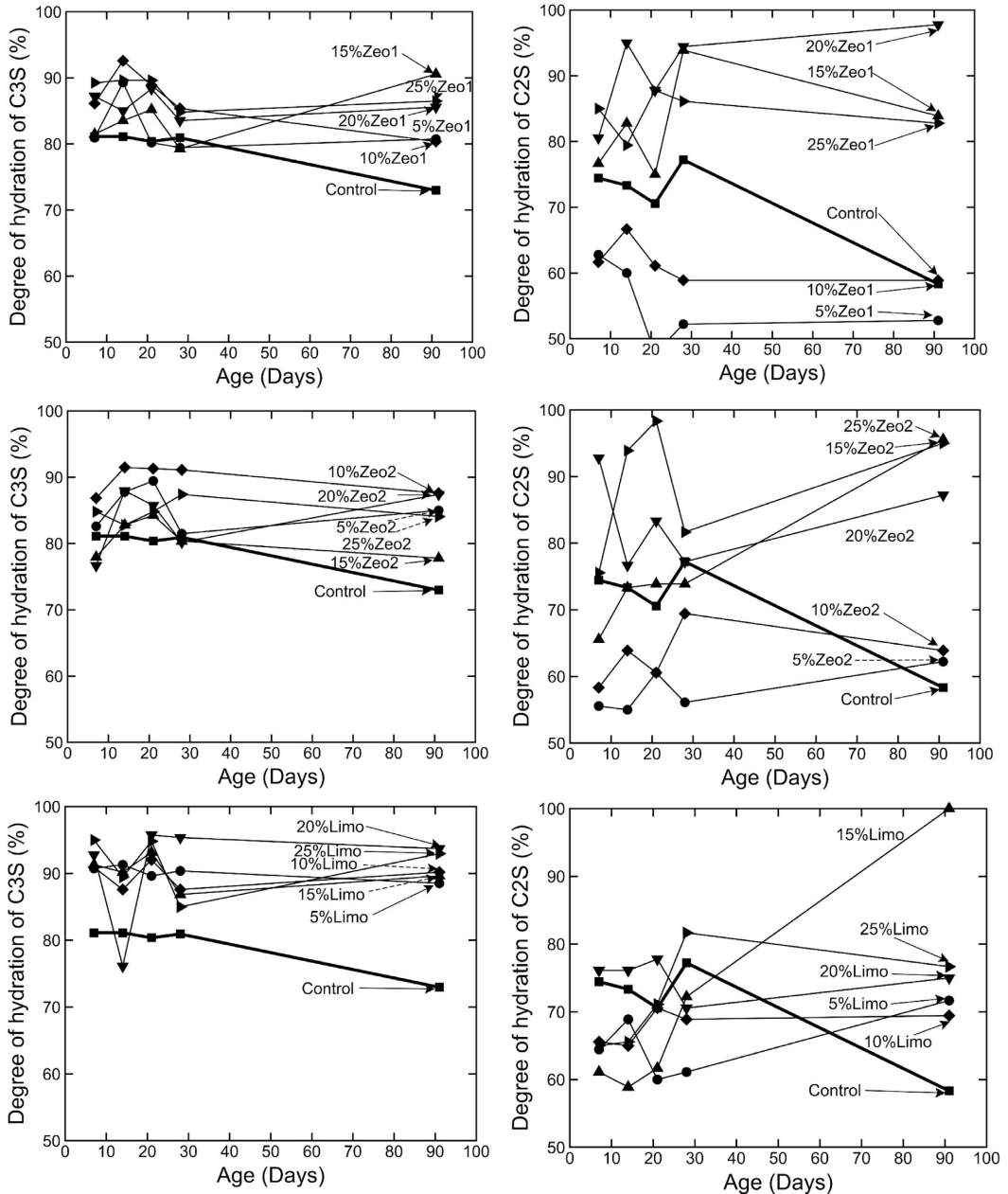


FIG. 2. Degree of hydration of C3S and C2S under air-curing conditions.

increase with time, probably due to self-desiccation, i.e. due to a decrease in the internal humidity during hydration (Igarashi *et al.*, 2004; Meddah, 2009; Zhutovsky & Kovler, 2012; Cornejo *et al.*, 2014) and the errors in the Rietveld method and with sample preparation (Scrivener & Fullmann, 2004; De la Torre & Aranda, 2011). Quartz (Qz) acted as an inert mineral addition throughout the hydration process; hence it scarcely reacted with hydrating cement phases. In contrast, neither Mor nor Hul-Cpt was detected after 7 days, suggesting that these zeolites were completely dissolved under the experimental conditions used. Moreover, a carbonate-like mineral was identified by XRD in all SCM-blended cement pastes even after 7 days and its abundance tended to increase slightly over time. The carbonate content was affected strongly by the dosage under air-curing conditions. As the replacement increased, so did the amount of calcite (Cc). Consequently, all blended cement pastes were carbonated with time. In summary, the main hydration products of the blended cement pastes were C-S-H and CH that were formed mostly up to 7 days, two un-hydrated cement phases (C3S and C2S) that were observed even after aging for 91 days and Qz, being a minor phase in the SCM, was also observed in association with the carbonate minerals during hydration.

The hydration of C3S proceeded fairly vigorously up to 14 days, but hydration of C2S had nearly ceased under the air-curing conditions, reaching only a maximum of 70% hydration; which might be explained by the dilution effect. Figure 2 shows that the degree of hydration of C3S in blended cement pastes was greater than for the plain cement pastes. With the W/B ratio of 0.3 deployed, without chemical additions, this behaviour can be interpreted as a combination of the accelerating effect of the SCM, yielding a greater amount of hydration products compared with the control sample (Kumar *et al.*, 2011; Lothenbach *et al.*, 2011) and by the water sorbed within the pores of the zeolites being available for further hydration (Ghourchian *et al.*, 2013). On the other hand, the degree of hydration of C2S was greater in the plain cement pastes than the blended ones with low cement replacement, but it was less in the plain cement pastes than the blended ones with high cement replacement (Fig. 2). The observed behaviour in pastes with low cement replacement, may suggest a greater effect of air curing on such a cement phase. However, the greater degree of hydration in pastes

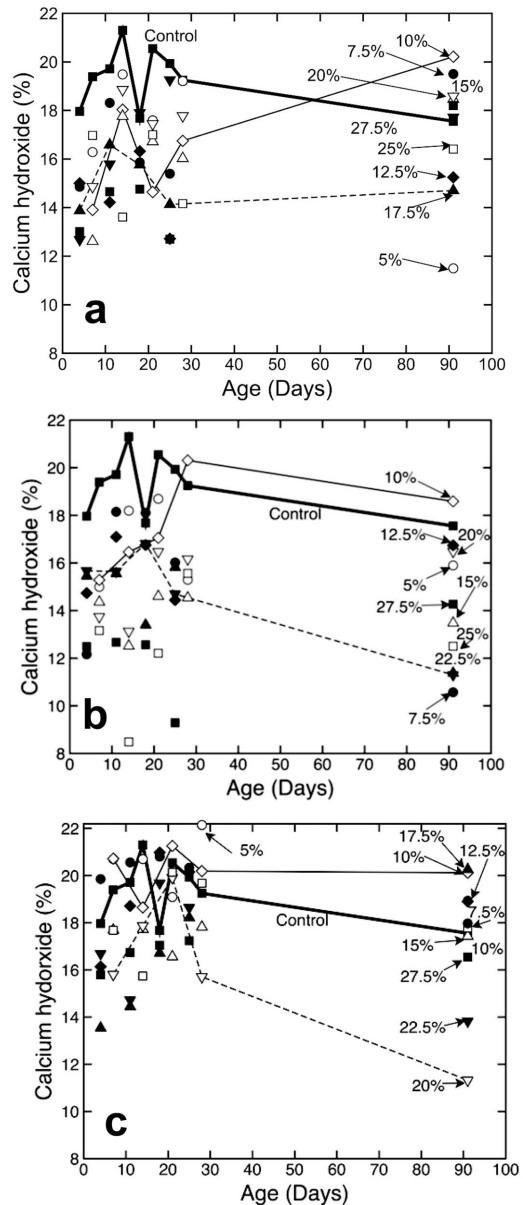


FIG. 3. Evolution of the CH content in blended and plain cement pastes under air-curing conditions over time. A: Zeo1, B: Zeo2, C: Limo. (Control – heavy line; Good performance mixture – light line; Poor performance mixture – dashed line).

with high cement replacement may possibly be due to a dilution effect. In summary, as C2S usually begins to hydrate at ~21–28 days, its hydration can scarcely proceed under these experimental condi-

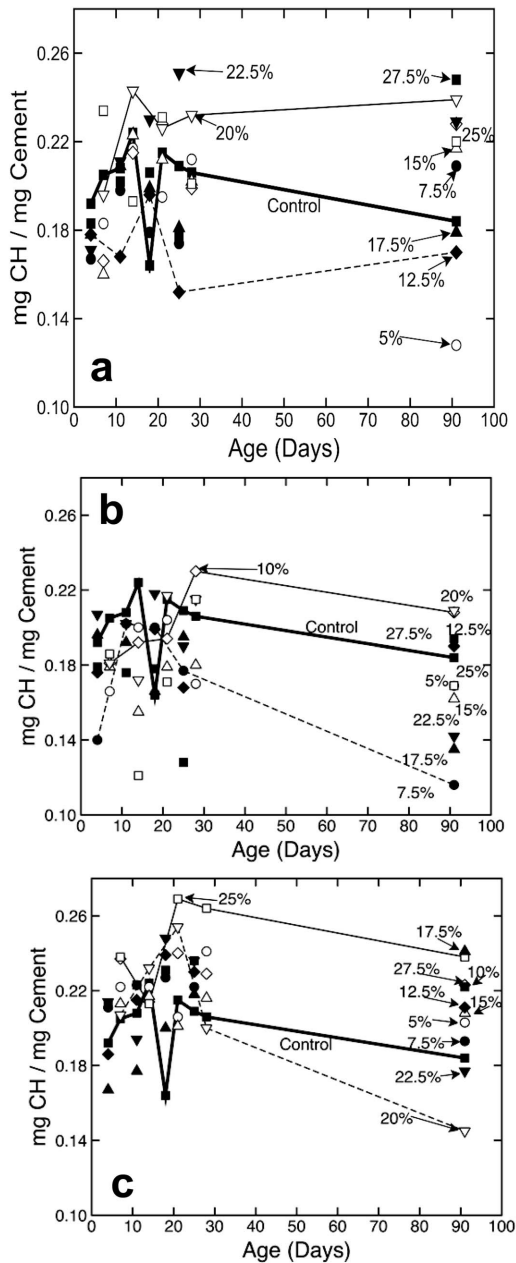


FIG. 4. Evolution of the ratio of CH content (mg)/ cement content (mg) in blended cement pastes under air-curing conditions over time. A: Zeo1, B: Zeo2, C: Limo. (Control – heavy line; Good performance mixture – light line; Poor performance mixture – dashed line).

tions as almost all of the water from the mixing process had already been consumed by the hydration of the C3S, mostly during the first 7 days. In this sense, the hydration of C2S produced hardly any CH in the absence of water.

In order to analyse the overall hydration, parameters such as the amount of CH, the ratio of mg of CH per mg of cement, the amount of calcite, the percentage of fixed lime, the degree of hydration, the normalized water in hydrates, as well as the density, were plotted for both validation and replication data. Discussion of these results follows.

In general, for low aging times, the CH content was greater in the control cement pastes than in their blended counterparts. Figure 3 shows the CH content for the blended cement pastes over time. Almost all Zeo2-blended cement pastes consumed the CH at a greater rate than the other cement pastes containing Zeo1 or Limo SCMs, keeping it at a lower level than that of the control pastes up to 91 days of aging. Nevertheless, some of the blended cement pastes containing Zeo1 or Limo had greater CH content than those of the control pastes in the longer term experiments.

After eliminating the dilution effect by normalization to the cement content, a number of blended cement pastes had a greater CH over cement-content ratio than the plain cement pastes (Fig. 4). This unexpected result could be due, in part, to the accelerating effect of SCMs over alite (C3S), the low W/B ratio and the air-curing conditions. Previous studies reported that blended cement pastes were able to produce more hydration products than plain ones at early ages (Ogawa *et al.*, 1980; Heikal *et al.*, 2000; Kakali *et al.*, 2000; Bjornström *et al.*, 2004; Korpa & Kowald, 2009; Kumar *et al.*, 2011; Eisinias *et al.*, 2012). Among others, the accelerating influence of zeolite tuffs and calcareous siltstone can be induced: by a filler effect (Heikal *et al.*, 2000; Bouasker *et al.*, 2008; Lothenbach *et al.*, 2011; Fernández and Martirena, 2011), by the presence of reactive silica (Fragoullis *et al.*, 1997; Talero & Trusilewicz, 2011), by the greater surface area of mineral addition (Fragoullis *et al.*, 2005; Korpa & Kowald, 2008; Cordeiro & Toledo Filho, 2011) and by the cation content and CEC of zeolites (Yilmaz & Ucar, 2007; Mertens *et al.*, 2009; Snellings *et al.*, 2010). At the same time this accelerating effect might be enhanced by the low W/B ratio (Gleize & Cyr, 2007; Ramezani-pour *et al.*, 2009). Finally, the air-

curing conditions might affect the plain cement pastes to a greater extent than the blended ones (Ozer and Ozkul, 2004; Sajedi *et al.*, 2012). In summary, as the amount of CH and other hydrates increased due to both the accelerating effects of the SCMs and the low W/B ratio at the early stages of hydration and because in the long term the air-curing conditions affected the plain cement pastes more than the blended ones, some of the blended cement pastes might retain more CH than the plain ones over the whole hydration process, in spite of the dilution effect.

As the amount of SCM increased, the carbonate content increased and an increase in the carbonate content was clearly notable between 28 and 91 days (Figs. 5, 6). The Zeo2 blended cement pastes generally contained larger amounts of carbonates than the Zeo1 ones. Moreover, the Limo-blended cement pastes had the largest carbonate content compared to the other SCMs; part of this calcite was a mineralogical constituent of the original SCM.

Plots of the percentage of the water content in hydrates normalized over the cement content are shown in Fig. 7. After normalization, the percentage of water content in hydrates was greater in blended cement pastes than in plain pastes. This might be related to the aforementioned accelerating effects of the SCM that increases the amount of hydrates in the blended cement pastes.

The hydration parameter also increased as the SCM dosage increased. As mentioned, previously, the accelerating effect of the SCM was enhanced at low W/B ratios and the effects of the air-curing conditions over plain cement pastes might lead to an almost direct relationship between the water in hydrates, normalized over the cement content, and the SCM dosage. Figure 8 shows a linear trend ($R^2 = 0.80$) between the percentages of water in the hydrates, normalized over the cement content, and the proportion of SCM added. The linear equation and its parameters for air-cured blended cement pastes in terms of water in hydrates, normalized over the cement content, are summarized in Table 2. Under air-curing conditions, an increase in the percentage of SCM by 1% on average, leads to an increase in the percentage of normalized water in hydrates (NHW) by 0.111%.

Fully-hydrated cement pastes may contain ~0.23 g of water per g of cement for the plain cement pastes (Brouwers, 2004; Hover, 2011). In this study, however, the plain cement paste with a W/B ratio of 0.3, cured in air, contained ~0.11 g of

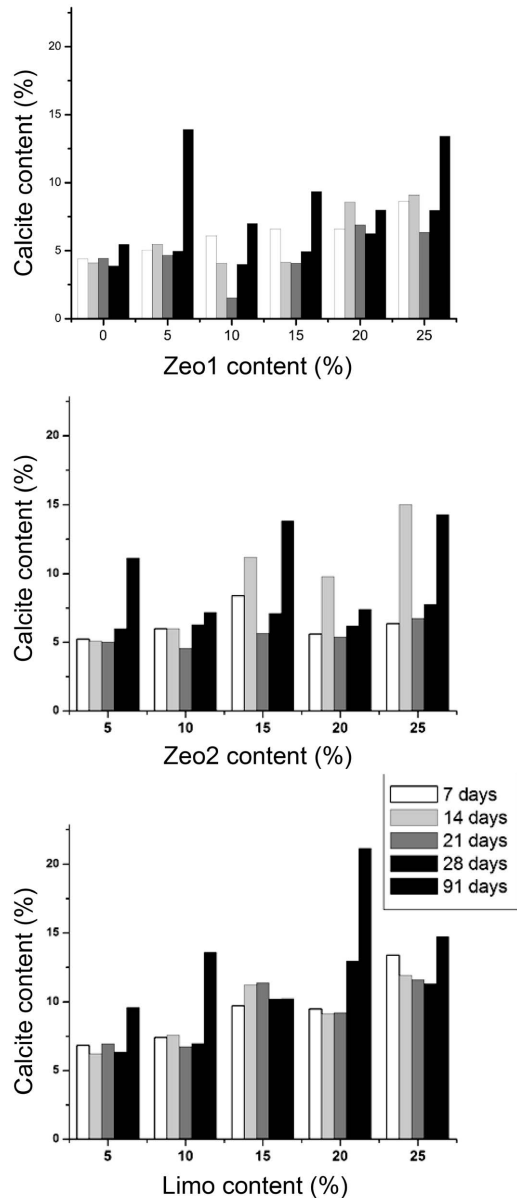


FIG. 5. Amount of calcite (Cc) in blended and plain cement pastes under air-curing conditions: Calibration.

water per g cement in hydrates after aging for 91 days. This means that ~50% of the total amount of water in fully hydrated cement pastes was used under air-curing conditions.

As the SCMs are less dense than the anhydrous cement phases, the density of the SCM-blended cement pastes decreased as the dosage increased

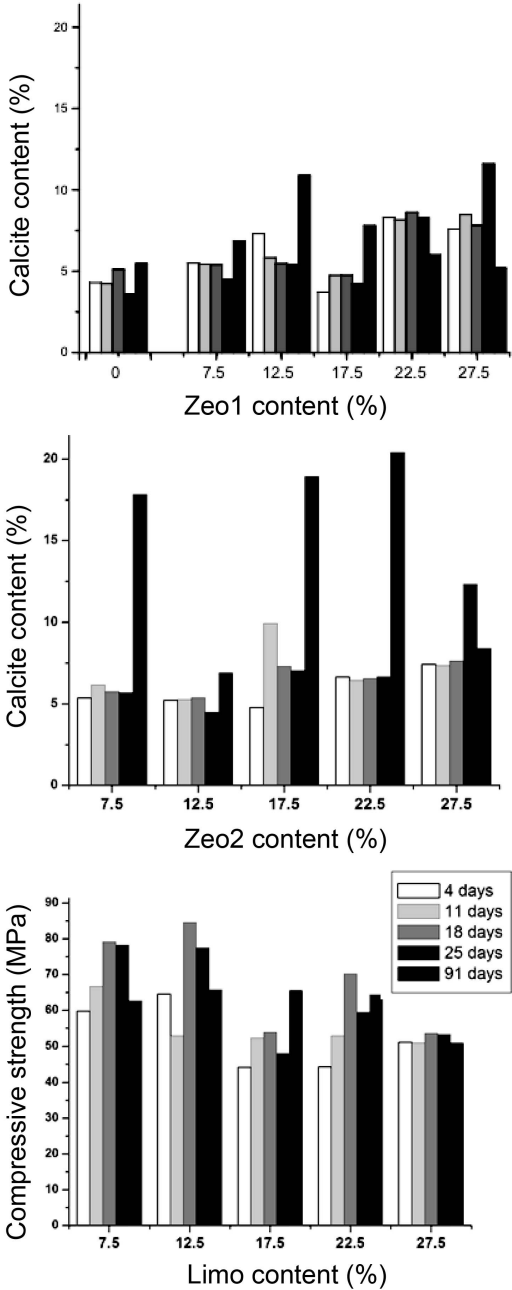


FIG. 6. Amount of calcite (Cal) in blended and plain cement pastes under air-curing conditions: Replication.

(Fig. 9). In addition, the density increased slightly over time, partly due to the formation of carbonates and hydration products, despite the lack of water for hydration. This suggests that the hydration did not

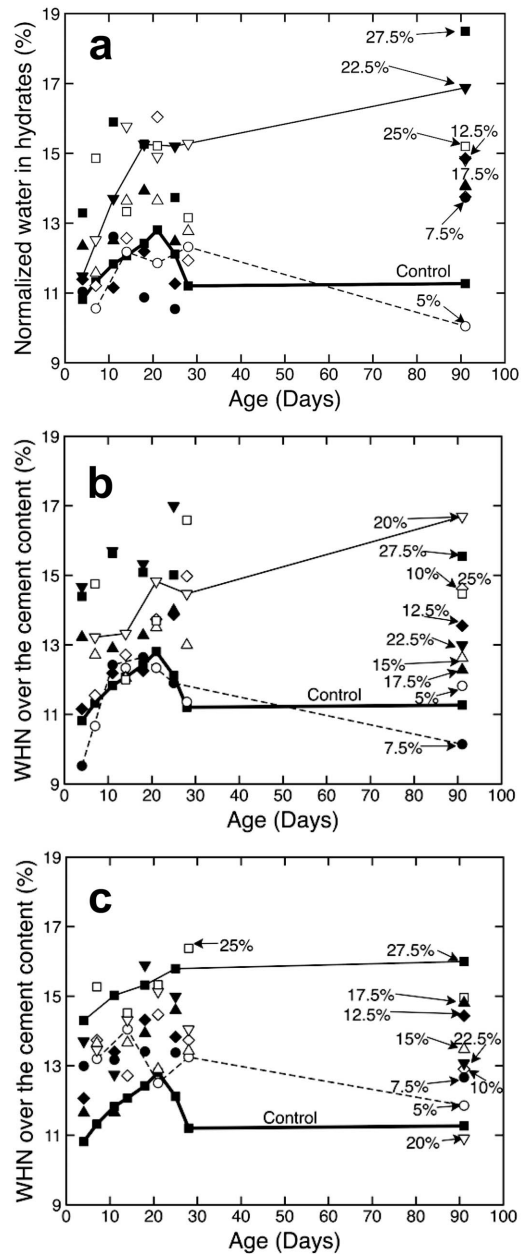


FIG. 7. Percentage of water content in hydrates normalized (WHN) to the replacement under air-curing conditions over time. A: Zeo1, B: Zeo2, C: Limo. (Control – heavy line; Good performance mixture – light line; Poor performance mixture – dashed line).

cease completely, but that “additional” water would be needed for hydration to be complete. In the case of natural zeolites, the zeolitic channels could be used

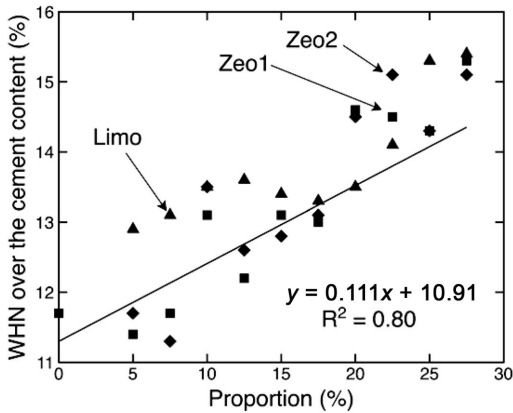


FIG. 8. Relationship between the percentages of normalized water in hydrates (WHN) and the proportion of SCMs in air-cured blended cement pastes.

as a water carrier (Snellings, 2012), although a recent study reported that natural zeolite aggregates might not supply sufficient additional water for complete hydration (Ghourchian *et al.*, 2013). In this case, zeolitic mineral additives with a smaller grain-size than aggregates, might release some additional water during the hydration stage. In addition to the zeolitic water, the hydration might continue via weakly-bound, non-evaporable water or via water bound to hydrates (Loukili *et al.*, 1999). Therefore, under these experimental conditions, the hydration did not cease completely as it appeared to consume all of the water available.

Due to the competing effects of the pozzolanic and carbonation reactions during hydration of these blended cement pastes, the ratio of the amount of CH consumed by each reaction was compared relative to the amount of cement used. All of the

TABLE 2. Slope (m) and intercept (b) of the linear equations for the percentage of the normalized water and the proportion of the different SCMs under air-curing conditions.

SCM	m	b
Zeo1	0.165	10.66
Zeo2	0.159	10.82
Limo	0.009	11.26
Average	0.111	10.91

$$NWH (\%) = 0.111 \times dosage + 10.91$$

values of the amount of CH consumed by the pozzolanic reaction were negative for both the calibration or replication samples, after aging for

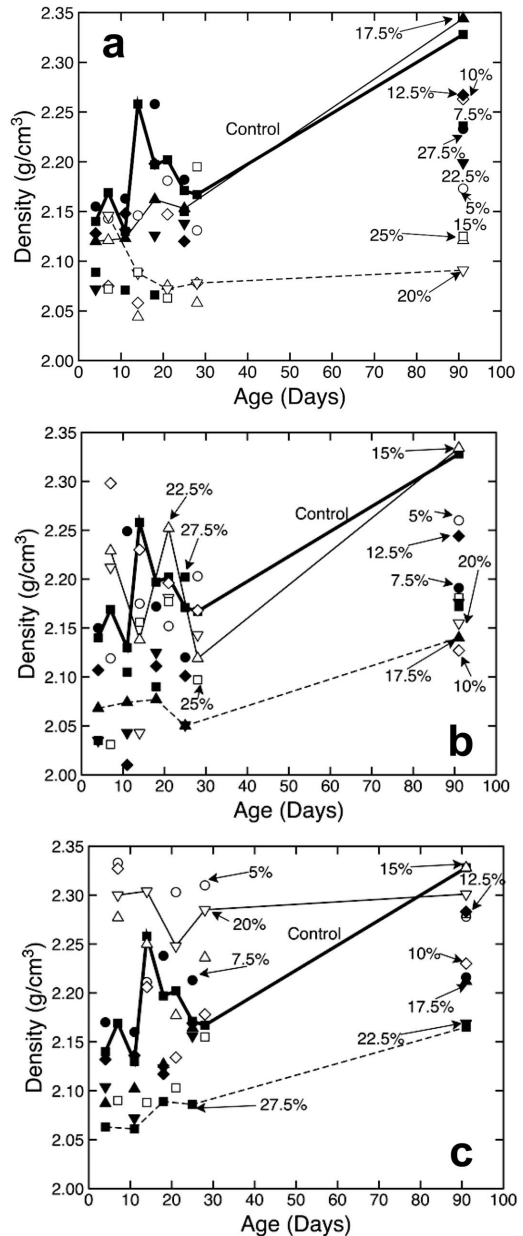


FIG. 9. Density of pozzolana-blended cement pastes under air-curing conditions over time. A: Zeo1, B: Zeo2, C: Limo. (Control – heavy line; Good performance mixture – light line; Poor performance mixture – dashed line).

91 days (Fig. 10), suggesting that the pozzolanic reaction scarcely proceeded under air-curing conditions at the low W/B ratio used. However, the reaction might have proceeded during the most

intense hydrating period before the 21–28 day interval. The Zeo2 additive showed greater pozzolanic activity than the Zeo1 during early aging, but later, this activity decreased steadily. In addition, the Limo sample, due to its low pozzolanic activity, did not show positive CH values because it did not fix the lime; instead, the carbonation reaction consumed the greater proportion of the CH.

The average percentage of carbonated CH after aging for 91 days was 45% of the total amount of CH that had been produced (Fig. 11). In all of the blended cement pastes the amount of carbonated CH increased over time. Therefore, the carbonation was more important for the consumption of CH than the pozzolanic reaction under air-curing conditions and at the low W/B ratio used. In addition, the control sample produced the least carbonated-CH over time, as the addition of SCM induced greater carbonation as the dosage increased. The carbonation probably proceeded beyond the time period monitored during these experiments.

In summary, for the low W/B ratio and air-curing conditions used, carbonation played the major role during the hydration, consuming almost half of the total amount of CH produced.

Effects of SCMs on compressive strength

After achieving high values of compressive strength over short aging-times, a decrease was observed (Figs. 12 & 13). In fact, only cement pastes blended with 20% Zeo1 showed a higher compressive strength than those given by plain cement pastes after aging for 28 days. All other blended cement pastes did not achieve values greater than those attained by the plain cement pastes over the whole experimental time. On the other hand, regardless of the type of SCMs, the lowest values of compressive strength were achieved for blends with high SCM-replacement, indicating that there is a negative effect of the high additive content upon the compressive strength under air-curing conditions. Hence, the mechanical performance was affected adversely by both air-curing and extensive replacement by SCMs.

In order to calculate optimum replacement values, a randomized block with one blocking factor was used for the experimental design summarized in Table 3. The optimal dosages for best mechanical performance were as follows: in the case of Zeo1-blended cement pastes, the optimal dosage was 5%; 20% dosage also showed a high

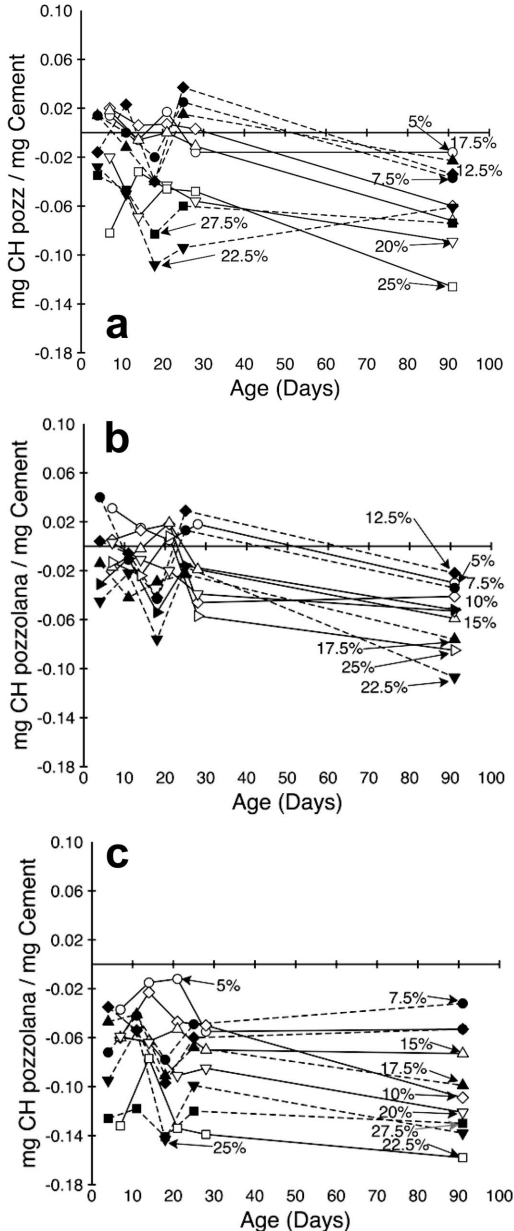


FIG. 10. Evolution of the amount of CH consumed in the pozzolanic reaction over time under air-curing conditions in the calibration and replication experiments. A: Zeo1, B: Zeo2, C: Limo.

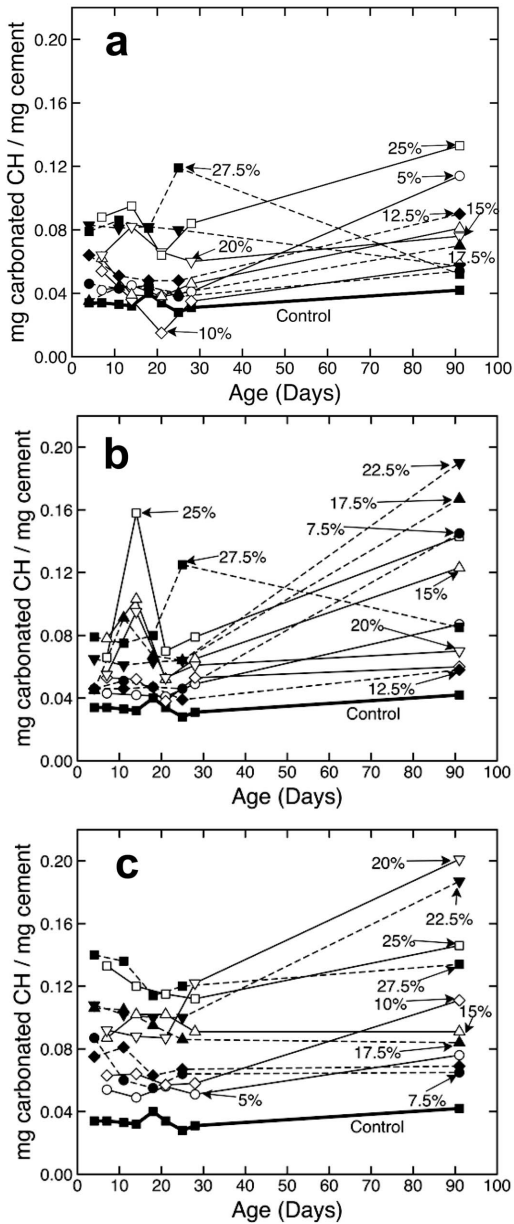


FIG. 11. Evolution of the amount of CH carbonated over time under air-curing conditions in the calibration and replication experiments. A: Zeo1, B: Zeo2, C: Limo.

value of compressive strength, as confirmed by the replication sample. In the case of the Zeo2-blended cement pastes, the optimal dosage was 5%, but 22.5% also showed a high value. In the case of the

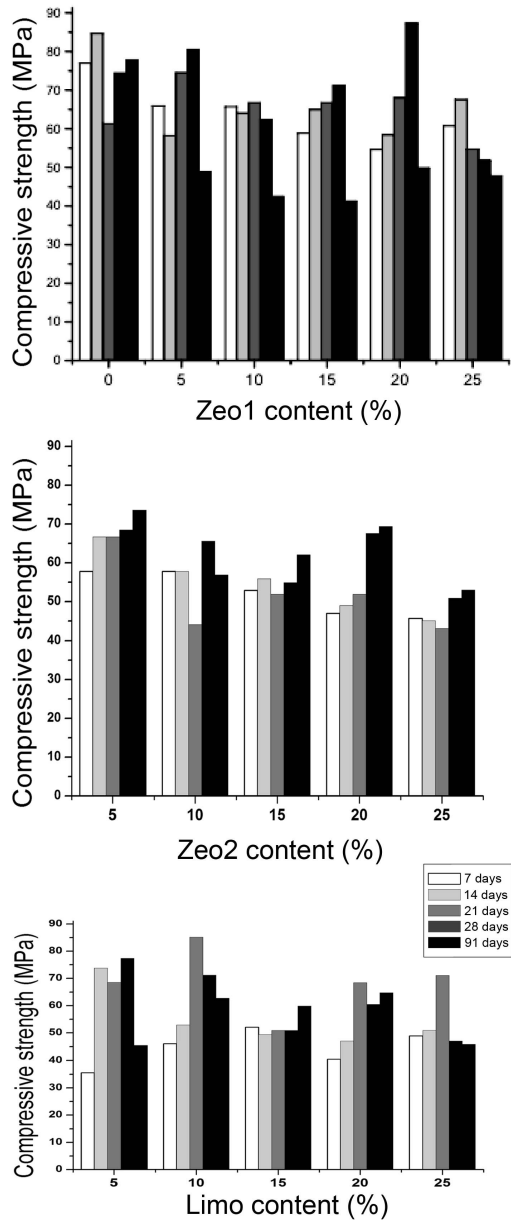


FIG. 12. Bar plots of the evolution of compressive strength of blended cement pastes under air-curing conditions over time: Calibration experiments.

Limo-blended cement pastes, the optimal dosages were 10–12.5%. Comparing the SCM-blended cement pastes with the controls, the plain cement pastes showed greater compressive strengths, in general, than the blended ones. In addition, the

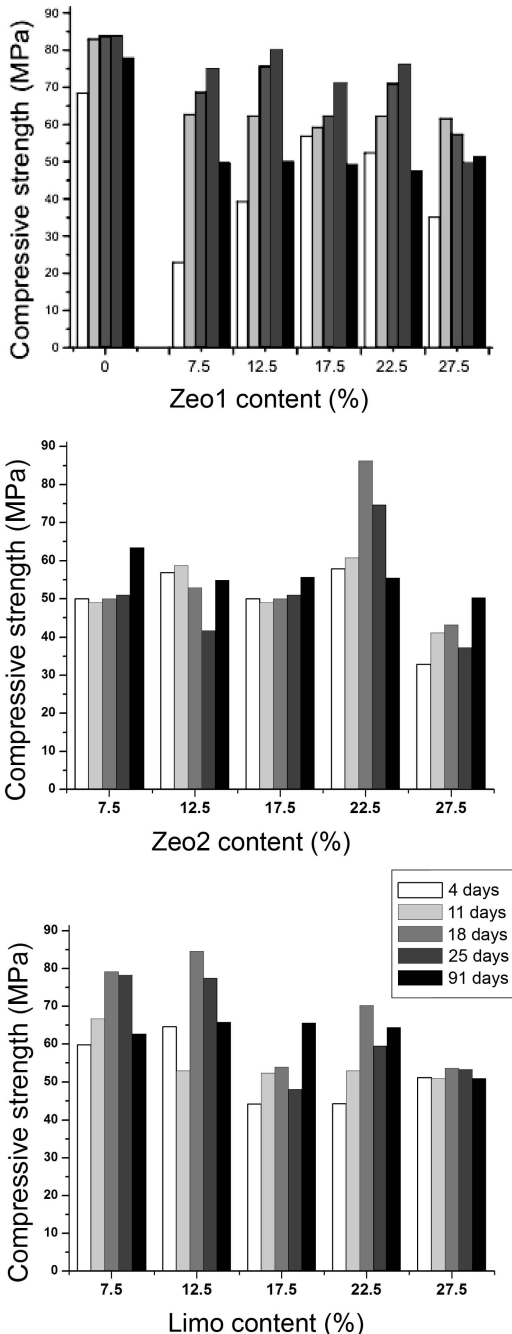


FIG. 13. Bar plots of the evolution of compressive strength of blended cement pastes under air-curing conditions over time: Replication experiments.

Zeo1- and Limo-blends had greater compressive strengths than the Zeo2-blends.

Although air-curing conditions affected the hydration products of both plain and low replacement cement pastes adversely, as they had greater amounts of un-hydrated cement phases and less CH remaining, they did show better mechanical performance. This might be due to the stiffening effect caused by the presence of significant amounts of un-hydrated cement phases, such as C3S and C2S, which can enhance the granular skeleton of the concrete (Loukili *et al.*, 1999). In addition, the high water-adsorption capacity of the zeolites may decrease the effective W/B ratio (Snellings, 2012), thus increasing the compressive strength. However, the carbonation, which is induced by extensive replacement with SCMs, may decrease the compressive strength; the effect being greater for the zeolite-blended cement pastes (Atis, 2004).

The microstructure was characterized by determining the apparent porosity of the matrix (Fig. 14). Seemingly, the pores increased with time. After 91 days, poorly defined crystals of CH were observed widely for blended cement pastes. In summary, these air-curing conditions mostly affected the microstructure partly because the original pore water was released.

CONCLUSIONS

The proportions of C3S, C2S, CH and CSH and the consumption of CH over time, by both the pozzolanic and carbonation reactions and their effects on the compressive strength of air-cured cement pastes were analysed successfully.

Several conclusions were drawn from this work:

Two stages of hydration were identified: (1) an early hydration stage that produced more than 97% of the total amount of CH and 98 % of the total amount of the CSH up to 7 days aging and (2) a mid-term hydration producing CH, CSH and other hydrates relatively slowly, as carbonation proceeded.

The amount of non-hydrated cement phases remained almost constant after 7 days and it was still possible to identify C3S and C2S after aging for 91 days, regardless of the addition of the SCMs.

The C2S phase was affected to a greater degree by air curing than the C3S. The degree of hydration of the C3S was greater over short aging times and the C2S did not react fully as almost all of the available water had been consumed during the hydration of the C3S.

TABLE 3. Least-squares-means with standard errors of the compressive strength (Mpa) for each proportion (%) of SCM and time of aging before testing (days), under air-curing conditions.

	Zeol1		Zeol2		Limo	
	Mean	Std. error	Mean	Std. error	Mean	Std. error
Calibration						
Control	75.68					
Grand mean	63.53	59.29	61.46			
Proportion%						
5	65.84		66.08		61.70	
10	59.58		55.80		66.33	
15	61.23	2.29	55.19	1.76	53.71	2.71
20	63.93		56.60		57.47	
25	54.93		46.40		53.88	
Age before testing (days)						
7	62.83		55.58		51.67	
14	66.42		59.54		60.63	
21	65.82	2.09	54.16	1.61	69.63	2.47
28	70.64		63.69		63.52	
91	51.94		63.50		61.85	
Replication						
Control	80.89					
Grand mean	61.31		57.62		64.33	
Proportion%						
7.5	56.24		52.52		69.28	
12.5	59.44		52.96		70.59	
17.5	58.54	2.23	51.64	1.94	53.43	2.00
22.5	61.29		67.34		58.82	
27.5	51.48		40.36		53.01	
Age before testing (days)						
4	46.65		52.69		56.38	
11	62.96		57.42		61.00	
18	69.72	2.04	61.33	1.78	72.08	1.83
25	72.25		56.19		72.08	
91	54.98		60.47		64.02	

The higher the dosage of the SCM, the higher the degree of carbonation, regardless of the type of SCM used.

The normalized CH content in blended cement pastes was generally greater than that in plain cement pastes. This might be due to a combination of: (1) the accelerating effect of the SCM over short aging times, (2) the negative effect of the air-curing conditions over the hydration of plain cement pastes or (3) the low W/B ratio used.

All blended cement pastes were able to fix lime, while hydration was proceeding, during the early stages. After achieving positive hydration values by

14–21 days, they shifted sharply to negative values, indicating that carbonation might have begun to compete for CH, a process not involved with the pozzolanic reaction.

The higher the SCM dosage, the lower the initial density of the pastes and the density increased slowly as hydration proceeded, suggesting that some hydrates were produced over the long-term. The percentage of normalized water in the hydrates increased as the SCM dosage increased.

Generally, the plain cement pastes showed greater compressive strengths and slower hardening rates than the blended cement pastes.

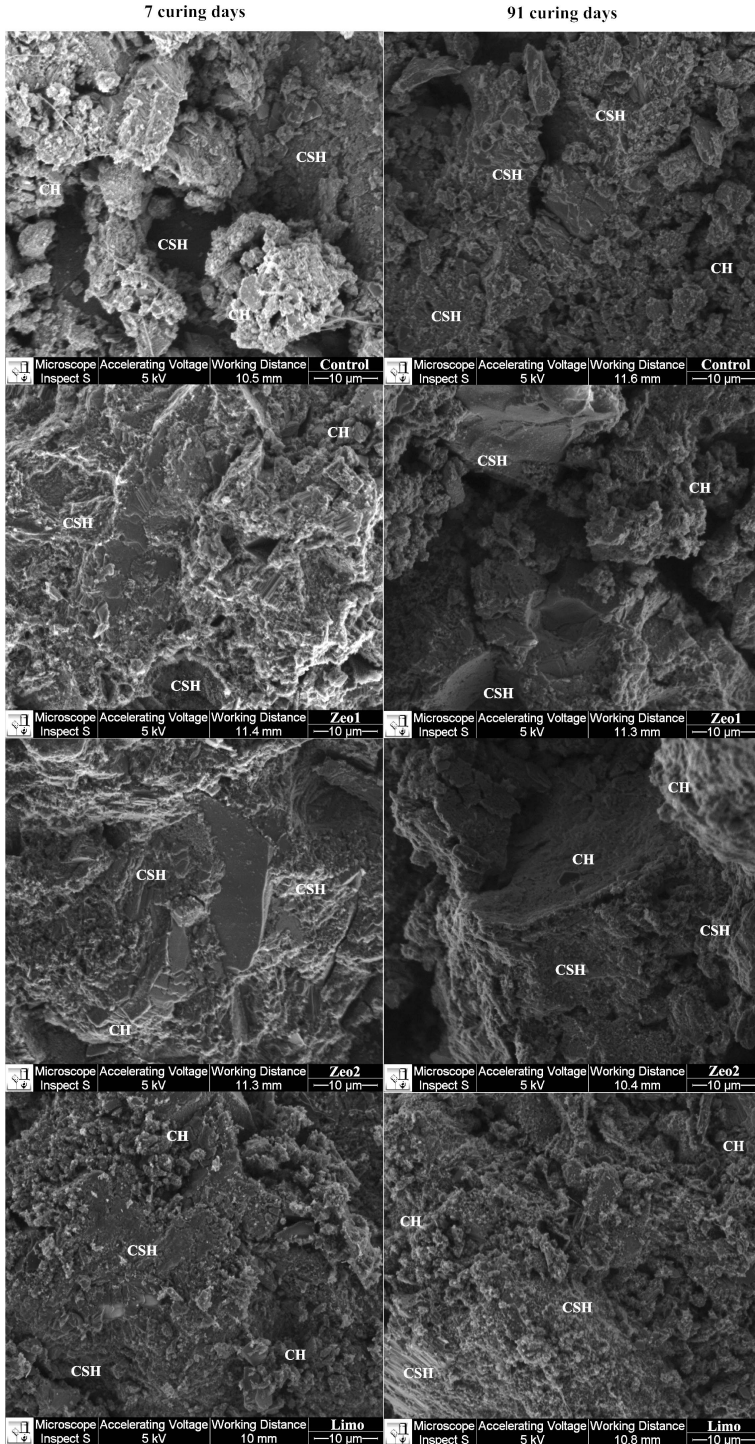


FIG. 14. SEM images of the specimens cured in air for 7 and 91 days in plain and Zeo1, Zeo2 and Limo cement pastes.

Air-curing conditions affected the mechanical performance to a lesser degree at lower SCM replacement, rather than at higher replacement, mainly after shorter aging times.

The Zeo1- and Limo-blends developed greater compressive strength than the Zeo2-blended cement pastes. For the Zeo1-blended cement pastes, the optimal dosage was 5%, although 20% also showed good values. For the Zeo2-blended cement pastes, the optimal dosage was 5%, but 22.5% also showed good values, while for the Limo-blended cement pastes the optimal dosages were 10–12.5%.

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