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Forced and natural carbonation of lime-based mortars with and without additives: Mineralogical and textural changes

G. Cultrone*, E. Sebastián, M. Ortega Huertas

Department of Mineralogy and Petrology, University of Granada, Avda. Fuentenueva s/n, 18002 Granada, Spain

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Abstract

We have studied the carbonation process in different types of mortars, with and without pozzolana or air-entraining additives, subject to a CO_2-rich atmosphere and compared the results with those of similar naturally carbonated mortars. We used X-ray diffraction technique to demonstrate that high CO_2 concentrations favour a faster, more complete carbonation process with 8 days being sufficient to convert portlandite into 90 wt.% calcite. Full carbonation, however, is not reached during the life-span of the tests, not even in forced carbonation experiments. This could be due to at least one of the following phenomena: a premature drying of samples during carbonation reaction, the temperature at which the carbonation process was carried out or the reduction of pore volume occupied by newly formed calcite crystals. This last option seems to be the least probable. We observed a more prolific development of calcite crystals in the pores and fissures through which the carbonic anhydride flows. Under natural conditions, carbonation is much slower and similar levels are not reached for 6 months. These differences suggest that the carbonation process is influenced by the amount of CO_2 used.

Both the mineralogy and texture of mortars vary depending on the type of additive used but the speed of the portlandite–calcite transformation does not change significantly. Pozzolana produces hydraulic mortars although the quantity of calcium aluminosilicate crystals is low. The air-entraining agent significantly alters the texture of the mortars creating rounded pores and eliminating or reducing the drying cracks.

Keywords: Mortar; Carbonation; $Ca(OH)_2$; $CaCO_3$; Petrography

1. Introduction and objectives

Lime mortars have been used as building materials since ancient times [1–3]. In the 19th century, the appearance of Portland cement led to a considerable fall in their use [4] because cement offered certain advantages such as fast setting and high mechanical resistance [5,6]. Lime mortars are now beginning to be used again in the restoration of historic buildings because they are compatible with traditional building materials [7–9], with which Portland cement shows low chemical and physical affinity [10,11]. Unfortunately in recent decades very little research has been done on lime mortars.

In terms of mechanical properties, lime mortar is capable of resisting some degree of movement in the masonry, but the stronger the mortar (i.e., that based on Portland cement) the less able it is to withstand this type of movement [12]. Another factor to be taken into account is the deterioration caused by salts from the alkalis normally contained in Portland cement [13,14]. Slow carbonation is one of the main factors in the decline in the use of lime-based mortars. Carbonation is of fundamental importance in making mortars harder and therefore more durable [10]. This process depends on many factors including relative humidity, temperature and CO_2 concentration [15–17] and normally involves an increase in mass caused by the transformation of portlandite into calcite [15,16]. It has been suggested that the total carbonation of mortar could take centuries [5,7].

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* Corresponding author. Tel.: +34 958 243340; fax: +34 958 243368.
E-mail address: cultrone@ugr.es (G. Cultrone).

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The study of lime mortar is gaining a prominent status among conservationists and conservation scientists involved in the safeguarding of our architectural heritage, however a better understanding of these materials is still required in order to be able to promote their use and develop better practice. In this work the evolution of high-CO_2 concentration during mortar curing was investigated and compared with natural carbonation. Our aim was to determine which mineralogical and textural changes were occurring in lime-based mortars because there are some aspects of this crucial process that are unclear and need more detailed research.

Moorehead [15] reported that the increase of CO_2 concentration during carbonate cementation increased the rate of the portlandite→calcite reaction. He also indicated that when 100% CO_2 gas is used, the heat generated during reaction (74 kJ/mol) is so great that a premature drying of samples occurs and not all the available lime is converted into calcium carbonate. The presence of water is another crucial factor in lime mortar carbonation. It is generated during reaction and it can be present as free or capillary water. Van Balen and Van Gemert [18] concluded that lime mortar carbonation depends on the presence of water and occurs very quickly on the outer surface, especially in a saturated CO_2 atmosphere, with a second phase of carbonation starting when the lime mortar has dried enough. Shih et al. [19] observed that a relative humidity of $<8\%$ did not permit the reaction of $Ca(OH)_2$ with CO_2 to form $CaCO_3$. And they report the independence of hydrated lime carbonation from CO_2 concentration. In contrast with this conclusion, Dehilly et al. [16] demonstrated the importance of CO_2 concentration during carbonation process. In fact, they observed how a lime paste underwent a rapid and complete reaction in a carbonic atmosphere, while in a low-CO_2 atmosphere carbonation took twice as long. A higher carbonation rate has been also observed in concrete when CO_2 content rises [20].

In our work, temperature and relative humidity were kept constant during the carbonation process, while the composition of the mortars was modified. A study was also made of how the presence or absence of certain additives affected the textural quality of mortars and the carbonation thereof.

We used both hydraulic and non-hydraulic lime mortars because both are commonly used in the construction industry. Pure lime mortars harden through a carbonation process only, whereas hydraulic lime mortars are denser and less fragile and to a certain extent resemble Portland cement mortars. Hydraulic lime mortars using natural pozzolanas were first used in ancient times by the Greeks and the Romans [21,22]. They are used today in the restoration of historical buildings because their chemical and physical properties are similar to those of the materials used by the original builders and because they ensure the development of superior mechanical properties, without having the general drawbacks of Portland cement. For this reason, a new volcanic ash was chosen to provide the mortars with the necessary hydraulic properties. Natural pozzolanas are known to be heterogeneous materials. Their reaction with lime is complex and depends on numerous factors such as their chemical composition, their degree of hydration and the morphology of the volcanic glass [23,24]. A study was made to see whether the selected volcanic ash reacted with hydrated lime and developed new calcium-silicate hydrate phases. This additive should be able to improve the durability of the mortars by increasing their mechanical resistance.

The durability of mortars once placed in a building fabric is influenced by external factors (i.e. environmental conditions) and by material properties (e.g. porosity, composition and texture [25]). A very common cause of deterioration is the formation of ice inside the porous system of mortars during freezing. This phenomenon is of great importance in countries where near-zero temperatures conditions are frequent. When water changes from a liquid to a solid state, its volume increases by 9% applying pressure of around 500 kg/cm^2 [26]. For this reason, an air-entraining agent was tested. These agents, which have only relatively recently come into use in the construction industry, improve mortar workability via the formation of air bubbles [27]. These bubbles are incorporated into the mortar and become part of the matrix that binds the aggregate together in the hardened mortar. It has been demonstrated that the introduction of minute air-bubbles dispersed uniformly through the mortar paste also increases mortar porosity, thus minimising damage caused by freezing in the masonry. In addition, an air-entraining agent could help to increase the durability of lime-based mortars subjected to salt weathering. The latter is commonly found in a range of environments [28–30].

2. Materials and methods

Four types of lime mortars (non-hydraulic and hydraulic) were tested against forced and natural carbonation by CO_2 (the abbreviation for each group of mortars is defined in brackets):

1) pure lime (L);
2) lime+air-entraining agent (LA);
3) lime+pozzolana (LP);
4) lime+pozzolana+air-entraining agent (LPA).

The weight percentage of additives was: 0.1% for the air-entraining agent (according to the recommendations of the manufacturer) and 20% for the pozzolana in accordance with the UNE 80-301-87 standard for cements [31].

A preliminary analysis of the lime, aggregate and pozzolana was made to determine their characteristics. The composition of the commercially available air-entraining agent is provided by the manufacturer.

2.1. Lime (binder)

The lime selected for these tests was an aged lime putty made by *Mazari de Época*, a manufacturer from Mollina in Málaga, Spain. The lime was stored under water for more than 18 years on rafts protected with plastic covers. A computerized laser assay (Galai CIS-1) revealed that in granulometrical terms, the lime had a high concentration of ∅≤1 μm particles (60% of total). Numerical percentages diminished concomitantly with an increase in size, there being virtually none over 25 μm (Fig. 1).

From a mineralogical point of view, lime is composed mainly of portlandite [$Ca(OH)_2$]. Low quantities of calcite (~10%) were detected. This was probably due to a partial recarbonation of portlandite during storage, handling or other manufacturing processes.

Mineralogical analysis was carried out using X-ray diffraction (XRD) with a Philips PW 1710 diffractometer with an automatic slit, CuKα radiation (λ=1.5405 Å), 3° to 60° 2θ explored area, and 0.1 2θ/s goniometer speed. XRD results were interpreted using the Xpowder program [32].

A thermogravimetric analysis (Shimadzu TGA-50H) was made to determine the structural and hydration water content of lime and any possible thermal decomposition of other mineral phases. The analysis was carried out in a flushed-air atmosphere (100 ml/min), using alumina (Al_2O_3) cells, a heating rate of 2 °C/min and an interval of 25–950 °C. Fig. 2 shows an initial weight loss until 110 °C, due to loss of the water added to the lime putty. This quantity represented 51.6% of the whole sample and this shows that the lime–water ratio was 1:1. A second weight loss of about 10.3% was observed between 400 and 478 °C caused by the loss of structural water present in portlandite. Another minimal weight decrease (less than 2%) was detected between 600 and 715 °C which may have been due to the presence of calcite, previously identified by XRD, decomposing into $CaO+CO_2$.

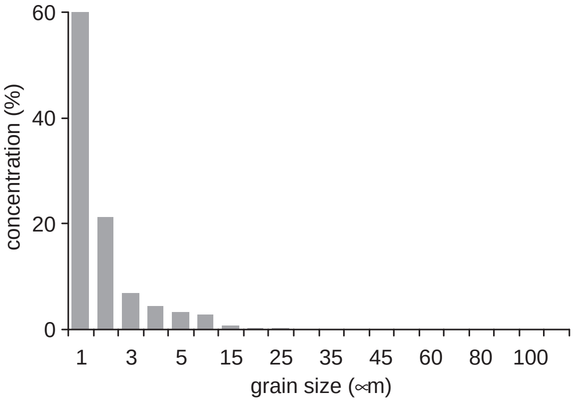

Fig. 1. Grain-size distribution of lime used in mortars. The horizontal bar represents the grain size (in μm) and the height shows the observed frequency.

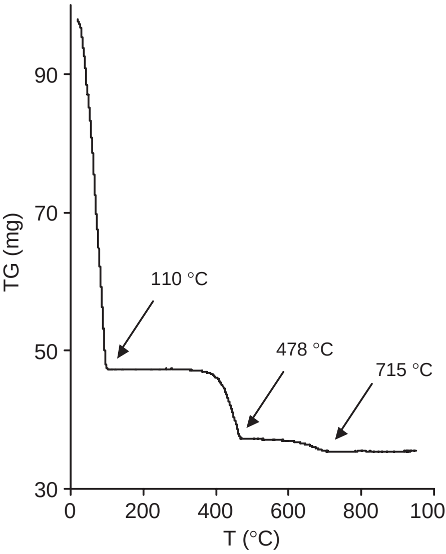

Fig. 2. Thermogravimetric analysis of lime. Temperature (in °C) versus weight loss (in mg).

Finally, bulk-chemical analysis was performed using X-ray fluorescence (Philips Magix Pro PW 2404). The estimated detection limit for major elements was 0.01 wt.%. 5 g of hydrated lime was packed into the Al holder for disk preparation. ZAF correction was made systematically [33] and international standards [34] were followed throughout. Particularly noteworthy in the chemical analysis is the high quantity of CaO (74.6%), 23.1% of CO_2 and very little MgO (1.2%) (Table 1). All other oxides show values of less than 0.4%. These data show that the lime is good quality material because the small size of the particles improves the union between them and the other components of the mortar during moulding and plasticity of the lime. The mineralogical composition (~90% of portlandite) is nearly ideal and favours a carbonation reaction that gives rise to a stable durable material.

2.2. Aggregate

The aggregate was a siliceous sand (0.05<∅<2 mm). This product is mineralogically and granulometrically certified by the Asociación Española de Normalización y Certificación (AENOR, Spanish ISO member). The estimated binder/aggregate ratio per volume was 1:3, because this is considered to be the best for restoration work [35].

2.3. Air-entraining agent

The selected air-entraining agent was a commercial product, Sikanol-M® (Sika, S. L). According to data provided by the manufacturer, it is an organic, fatty alcohol derived, plasticising air-entraining agent of normal setting characteristics and ready for use with all types of mortars. It is sold in the form of a brown, not very viscous liquid (ρ=1.06 g/cm^3), free of chlorides and with a pH=8.00

Table 1
Bulk composition of lime and pozzolana (XRF results in wt.%; Zr in ppm)

Sample	SiO_2	Al_2O_3	Fe_2O_3	MnO	MgO	CaO	Na_2O	K_2O	TiO_2	P_2O_5	SO_3	Cl	Sr	CO_2	Zr
Lime	0.29	0.12	0.06	–	1.21	74.61	0.03	–	–	0.07	0.38	0.03	0.01	23.10	189.30
Pozzolana	46.61	16.55	12.01	0.18	6.14	10.62	2.83	1.92	1.71	0.53	–	–	–	–	

–: not detected.

(additional details can be found in: www.sika.es). The colour of the product did not affect that of the mortars since the dosage used was very low (0.1 wt.%).

2.4. Pozzolana

The volcanic ash used to prepare the hydraulic mortars comes from Mount Etna in Sicily, Italy.

The minerals detected included plagioclase and pyroxene, plus an amorphous phase (volcanic glass) detectable by a rise in the background noise in the XRD pattern.

In chemical terms, this volcanic ash falls into the hawaiite field, a typical composition of past and present-day volcanic activity of Mount Etna [36,37], with ~17% CaO+MgO content, ~47% SiO_2 concentration, and 16% Al_2O_3 (Table 1).

Prior to the moulding of the lime with volcanic ash, the size of the pozzolana particles was reduced by grinding the ash in a wolfram mortar for 10 s to increase its specific surface and reactivity. As a result, a particle range of 35–130 μm (particles <35 μm represented only 7% of the total) was reduced to 1 to 15 μm and, most strikingly, the maximum size fell by 4 μm (Fig. 3).

2.5. Experimental procedure

All the mortars were moulded mechanically for 20 min using an ICON automatic mixer. They were then put into PVC tubes (15 for each group) that were 5 cm tall and 3 cm in diameter. The tubes were filled to half-full. Mortars were gently squashed down to compact them. While they were drying off, they were weighed periodically with extremely sensitive A and D ER-120A scales which have an accuracy grading of 0.0001 to 120 g. According to Van Balen and Van Gemert [18], it must be emphasised that when mortar samples are drying (which causes a weight loss), an incipient carbonation process occurs (and weight increases). After 10 days, almost constant weight was reached (although the samples had not dried out completely), and forced carbonation was carried out.

The carbonation of the lime-based mortars was done in a Kesternich weather chamber with a useable volume of 200 dm^3 (Fig. 4), at a constant temperature of 25 °C and a relative humidity of 50%. 1.25 dm^3 of CO_2 was introduced into the chamber for 10 min. Every 48 h the chamber was opened and two samples from each group were collected and weighed on the electronic scales. The other samples were saturated with CO_2 again in the chamber. When no more changes in the weight of the samples could be detected, the test was considered to have finished.

During this test, the carbonation process was mineralogically and texturally controlled by means of XRD (two samples for each group of mortars, ~1 g each), optical microscopy (OM, OLYMPUS BM-2) and a field emission

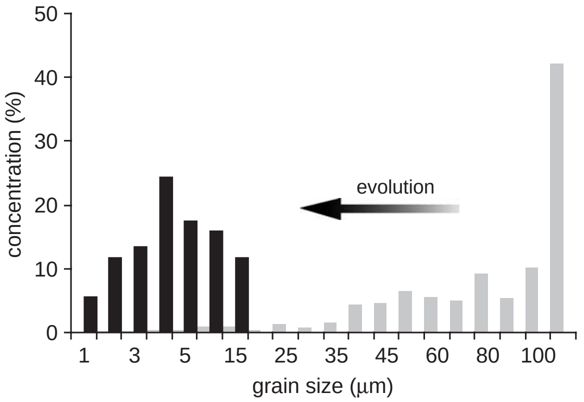

Fig. 3. Grain-size distribution of pozzolana before and after grinding (grey and black columns, respectively). The arrow shows the particle size development.

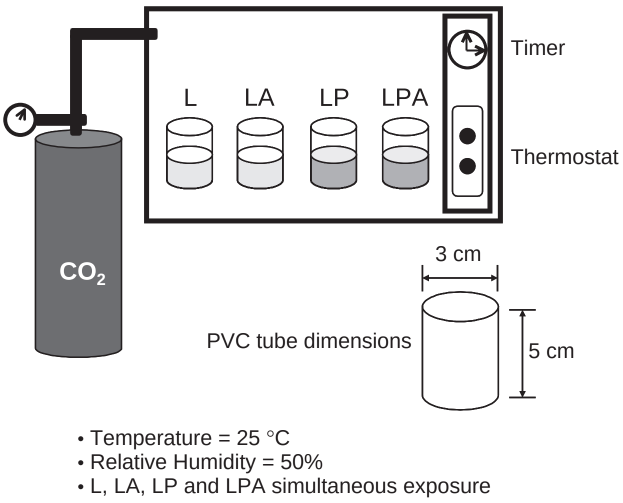

Fig. 4. Diagram of the Kesternich chamber for the forced carbonation of mortars.

scanning electron microscope (FESEM; LEO GEMINI 1530) coupled with INCA-200 Oxford microanalysis. Semiquantitative analysis of portlandite and calcite was performed using the experimentally determined reflectance power of these phases, according to Culliti's method [38]. Two thin sections per sample type, submitted to 1 month's forced carbonation, were prepared for OM observations. FESEM secondary electron (SE) and back-scattered electron images (BSE) were obtained using small mortar pieces (5×5×10 mm; carbon coated), or polished thin sections (carbon coated).

Finally, to be able to compare quick carbonation with the natural carbonation of mortars, a group of samples similar to the previous ones were prepared and carbonated outside the chamber at the same temperature and relative humidity conditions.

3. Results and discussion

3.1. Weight increase

After 30 days all the samples subjected to forced carbonation registered weight increases of approximately 6% (at which time it was decided to stop the test as no further weight changes were discernible in the mortars). The highest values were for the L group (6.6%) and the lowest for the LP group (5.7%). The lower values registered by LA and LPA mortars if compared with the L group can be explained by the fact that the air-entraining agent generates highly porous mortars with a low degree of interconnection between pores [39]. Pores are poorly connected thus hampering the movement of water (and gas) inside the mortars. It is important to note that after 8 days all the samples had already reached their maximum weight, and subsequently showed only small oscillations (Fig. 5a).

If we compare these results with those provided by the mortars subjected to a process of natural carbonation, we can see that after 20 days the latter mortars had still not reached a 0.5% weight increase and after 4 months the percentage was 1.75% for L and LA and 1.30% for LP and LPA. It can therefore be deduced that if the rate of weight increase were similar to that registered during the first days of this test, it would take 1 year to obtain the same results as achieved with the samples carbonated in the weather chamber (Fig. 5b). Nevertheless, the rate of weight increase always slowed down concomitantly with time. This gave rise to an asymptotic curve when $\Delta M/M<3$ which corresponds to less than half the weight increase of the mortars subjected to forced carbonation. At the moment, after 6 months, the weight of the mortars is still rising, albeit very slowly. One should bear in mind that all samples (forced and naturally carbonated) started to carbonate during the drying phase as described in Section 2.5. The weight difference already shown by these two groups of mortars at 2 days of carbonation suggests that the amount of calcite generated before the beginning of this test would have been very limited. Taking into account that temperature and relative humidity were the same for both forced and naturally carbonated samples, the CO_2 concentration during the carbonation process emerges as a crucial parameter in lime mortar carbonation kinetics. At higher CO_2 concentration, the excess CO_2 (i.e. CO_2 molecules that have not already reacted with available hydrated lime) can penetrate deeper into the mortar block, thus producing a thicker carbonated area (leading to faster carbonation). At atmospheric CO_2 concentration, any CO_2 molecule entering the mortar pore system could rapidly react with $Ca(OH)_2$ (upon CO_2 dissolution in pore mortar). Thus all CO_2 molecules will be "trapped" in the mortar near-surface, before the reaction front progresses to the sample core (i.e. the mortar acts as a sink for CO_2). This makes sense considering that $Ca(OH)_2$ is used as a gas stripping agent for CO_2. As long as there is unreacted $Ca(OH)_2$ on the surface layer, the carbonation front will not move towards the core of the mortar.

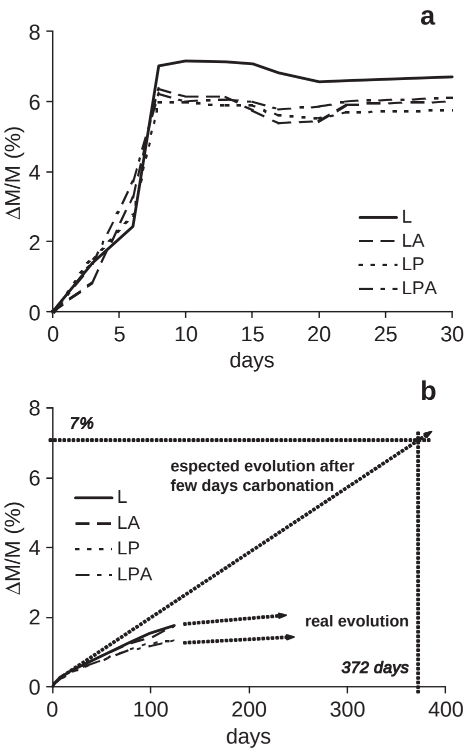

Fig. 5. Mortar behaviour during forced carbonation: (a) weight gain (in %) during forced carbonation *versus* days of mortars without additives (L) and with air-entraining agent (LA), pozzolana (LP) and pozzolana+air-entraining agent (LPA); (b) weight gain (in %) during normal carbonation versus days of L, LA, LP and LPA mortars.

Note that the reaction rate will be independent of CO_2 concentration. The rate will depend on the reactivity of the lime (i.e. surface area) and the water content [18]. Nonetheless, even in the event of a constant reaction rate, the higher CO_2 concentration will lead to faster, more thorough carbonation.

Bearing in mind the molecular weight of portlandite (74.09) and calcite (100.09) and the densities of portlandite (2.23 g/cm^3) and α-quartz (2.53 g/cm^3), and considering that in these mortars three parts are occupied by the aggregate (α-quartz) and one by the lime, a weight increase of 7.91% can be calculated if complete transformation of portlandite into calcite occurs. The 6% measured in experiments on forced carbonated mortars corresponds, therefore, to 75.85% carbonation of the initial mass of the lime. Furthermore, if we consider that the lime putty used was not wholly made up of portlandite (10% inert calcite was detected), the increase in weight observed brings us close to complete carbonation of these mortars. On the other hand, a ~1.5% weight increase measured in naturally carbonated mortars indicates only 20.23% carbonation.

3.2. XRD

It can be seen in Fig. 6, which shows the graph of XRD semiquantitative analysis with regard to calcite concentrations in the mortars versus the time of carbonation, that there is a clear link with the results obtained by weight increase (Fig. 5a); in general and for samples subjected to forced carbonation, L group reaches the highest degree of carbonation. In detail, it was observed that, after 2 days, more than 50% of the portlandite had turned into calcite. An unquantifiable part of this calcite crystallizes during the drying process but, as indicated in the previous section, this amount would seem to be very low. After 6 days the weight percentage of $CaCO_3$ was nearly 65% and after 8 days it was over 90%. This shows that almost all the mortar had carbonated after 8 days in a CO_2-saturated atmosphere, as weight increase data suggested. It should be remembered that this type of XRD semiquantitative analysis has conditioning factors that produce a ±5% margin of error [40]. However, this error is of lesser importance, as here we are comparing results of different samples, analyzed under similar conditions. It is also clear that a 100% calcite value has not been reached. The complete transformation of $Ca(OH)_2$ into $CaCO_3$ is difficult to obtain. It may be due to the heat produced during the transformation of portlandite into calcite. The capillary water inside the mortars can evaporate, especially when high CO_2 concentrations are present [15]. This first hypothesis can explain why the reaction in forced carbonated samples ended after only 8 days while in naturally carbonated mortars it is still going on. In fact, numerous references point to the very long periods of time required to obtain the complete carbonation of lime mortars under natural conditions [5,7]. A second factor that can impede or at least reduce the reaction is the temperature at which the test is carried out. Dehilly et al. [16] observed the complete carbonation of portlandite probably because of the lower temperatures they used in their research. It is known that the solubility of CO_2 decreases as temperature increases [15]. Another cause could be the reduction in porosity during carbonation as a result of calcite crystallization which reduces the space through which gas molecules can migrate towards the calcium hydroxide crystals located inside the mortar [23].

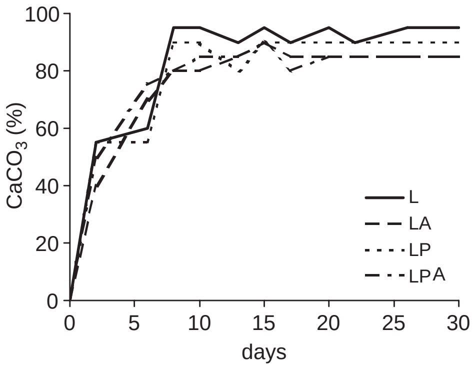

Fig. 6. % of newly formed calcite during forced carbonation versus days of L, LA, LP and LPA mortars.

The pattern of the XRD diffractograms at 48 h and after 1 month of forced carbonation (Fig. 7) shows the quantitative variations in the mineralogy of the mortars. After 2 days practically half the portlandite (Po) present in the mortars had carbonated. The carbonation could start during the earlier drying phase, but contact with a CO_2-rich atmosphere (and, of course, the presence of water) is what accelerates the process. In fact, a comparison with the limited weight increase of samples subject to natural carbonation confirms this assertion. After 30 days the value for portlandite was around 10–15% compared to the carbonates in the samples, although, as mentioned above, after just 8 days the percentage of this mineral phase was practically the same.

It should be mentioned that XRD was unable to detect in LP and LPA (Fig. 7) the calcium aluminosilicates that are normally formed when lime comes into contact with volcanic ash. This is probably because the quantity produced was below the detection limit for this technique.

3.3. OM

Optical microscope observations show how the union between binder and aggregate is continuous and complete, indicating that the mortars are well cemented.

The morphology of the quartz grains ranges from subangular to round. The calcite is micritic. The appearance of the mortars varies depending on the additive used. In the case of mortars without additive (L), some irregular-shaped pores and some drying cracks can be seen (Fig. 8a). The air-entraining agent (LA) produces very porous mortars but there are no retraction fissures. The pores are round and <100 μm in size (Fig. 8b). The presence of pozzolana produces a change in the colour of the binder, which turns from white to grey. The particles of volcanic ash are not recognizable, however, because they are very

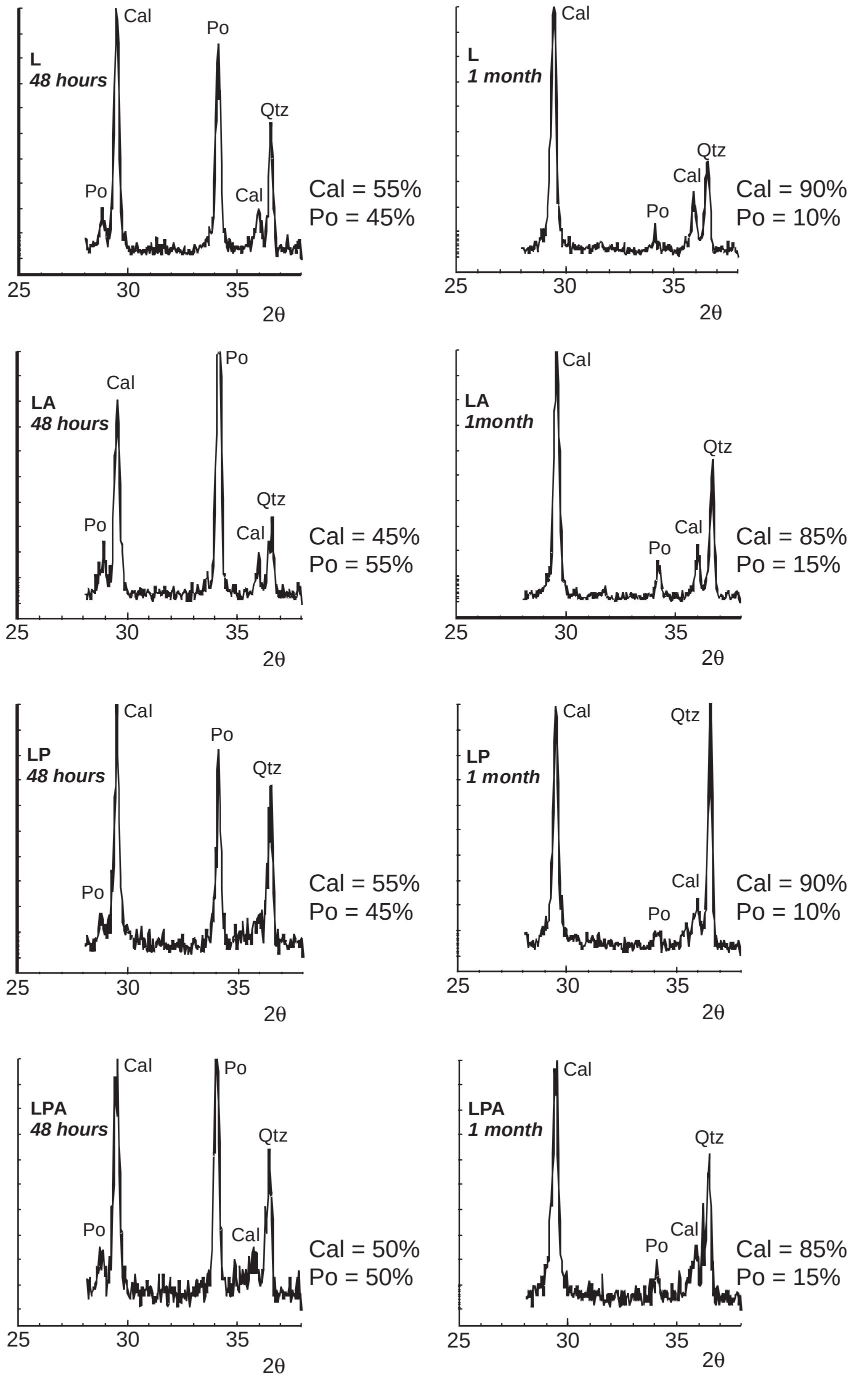

Fig. 7. L, LA, LP and LPA mortar-sample powder-X-ray-diffraction patterns at 2 and 30 days of forced carbonation. 28 to 38° 2θ explored area. Legend: Po=portlandite; Cal=calcite; Qtz=quartz.

small (∅=1–15 μm). As in the two previous mortar groups, the pores in LP (Fig. 8c) are angular while in LPA they are rounded (Fig. 8d).

3.4. FESEM

Lime carbonation leads to changes in the morphology of the crystals. After 2 days of exposure to CO_2, numerous pseudo-hexagonal, plate-like crystals of portlandite were still visible. In some cases they were isolated, and in others they were heaped on top of each other (Fig. 9a). These crystals were very small in size, ranging from 200–300 nm to 1 μm.

After 4 days, the number of portlandite platelets fell slightly and they were replaced by calcite crystals of irregular morphology (Fig. 9b). This replacement was accentuated after 8 days' forced carbonation. In Fig. 9c, it can be seen that the surface of L mortars was covered by 1-

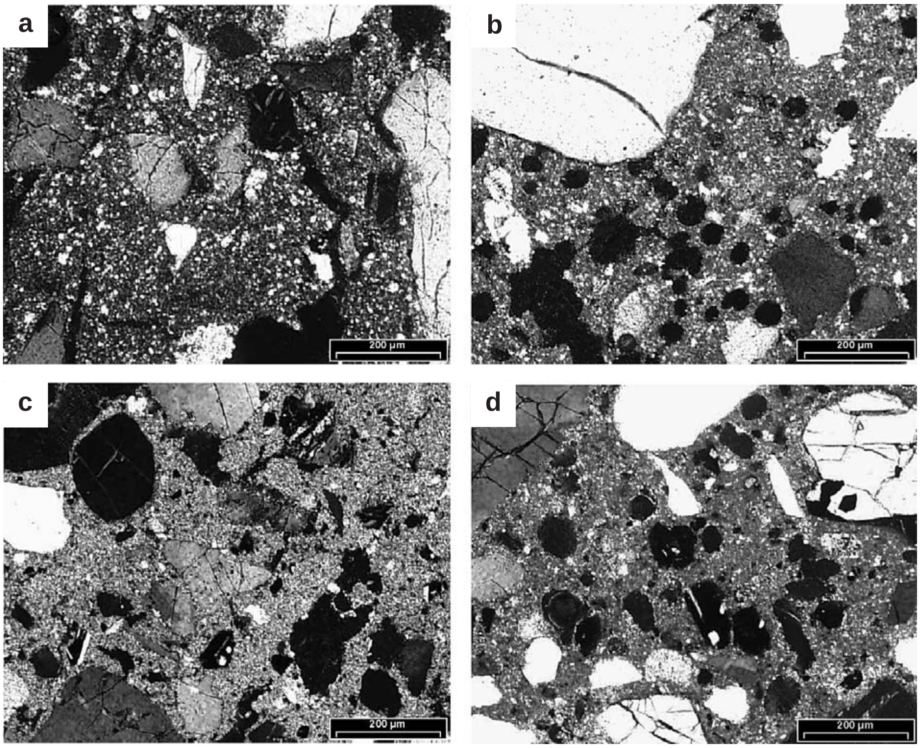

Fig. 8. Optical-microscope microphotographs of L (a), LA (b), LP (c) and LPA (d) mortars.

µm-wide scalenohedral calcite. After a month, there were just a few portlandite crystals left dispersed among the calcite crystals which were generally twinned in a rosette-like shape (Fig. 9d).

Texturally, the pores in the mortars are irregular in shape, not fissural. They are well connected to each other although they seem to get smaller as carbonation increases. This is a logical phenomenon since the reaction of calcium hydroxide with carbonic anhydride to form calcium carbonate is accompanied by a need for more space for the calcite crystals, calculated at almost 12% [15,41]. Thus the decrease in the space accessible to the water led to a

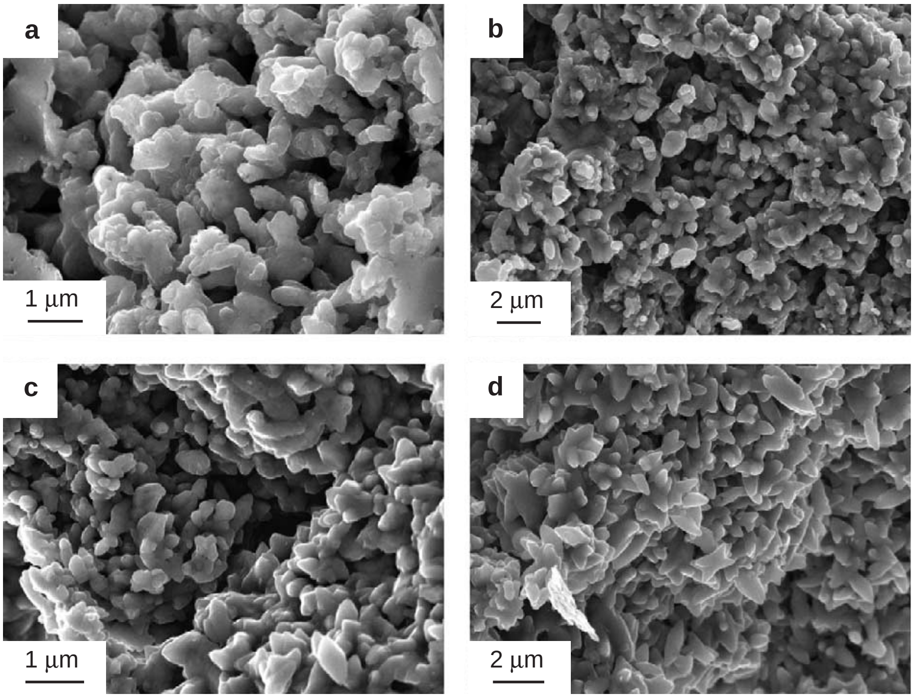

Fig. 9. SEM secondary electron microphotographs of L mortars at 2 (a), 4 (b), 8 (c) and 30 (d) days of forced carbonation.

reduction in the open porosity of the mortars and theoretically to an increase in their mechanical resistance [42]. However, the pores are still large enough to allow CO_2 diffusion. This observation therefore rules out (or at least makes quite improbable) the hypothesis discussed above of incomplete carbonation due to a reduction of porosity.

Some differences could be found when comparing the mortars with and without additives. The role of the air-entraining agent is to increase the porosity and above all the number of macropores and this property is confirmed by sample LA (Fig. 10a) where there are larger pores than in the other types of mortar. After 4 days' forced carbonation (Fig. 10b), portlandite platelets and several calcite crystals were identified both on the surface and inside the LA mortar. Fig. 10c shows the appearance of a "*hydraulic mortar*" (LP) in which the particles of volcanic ash (white arrow) are completely covered by calcite crystals (Fig. 10d), suggesting an incipient reaction between the lime and the pozzolana. Finally, the use of either type of additive produced a quite porous mortar (Fig. 10e, LPA sample) in which pozzolana particles could be identified. At high magnification (Fig. 10f), calcite crystals covering the surface and volcanic ash particles were visible.

BSE images of the mineral and textural composition of samples with and without additives give an interesting picture of some aspects of phase transformations. Fig. 11a shows the morphology of the quartz crystals (Qtz) in the LP mortar. Retraction fissures can be detected with a thickness of ≤10 μm and the pores are irregular in shape. At greater magnification a small mass of poorly kneaded lime (50 μm wide) can be observed in the matrix of the LP mortar, something which occurs only rarely in these mortars (Fig. 11b). Microanalyses of the matrix show the existence of the lime–pozzolana reaction that creates new calcium silicates, although it is impossible to identify the specific developed phase. There are not enough of these newly formed mineral phases for them to be detected by XRD. As Radonjic et al. [6] suggested, it is possible that calcium silicate phases formed initially were not stable under high-CO_2–water exposure, and were therefore partially destroyed. In these

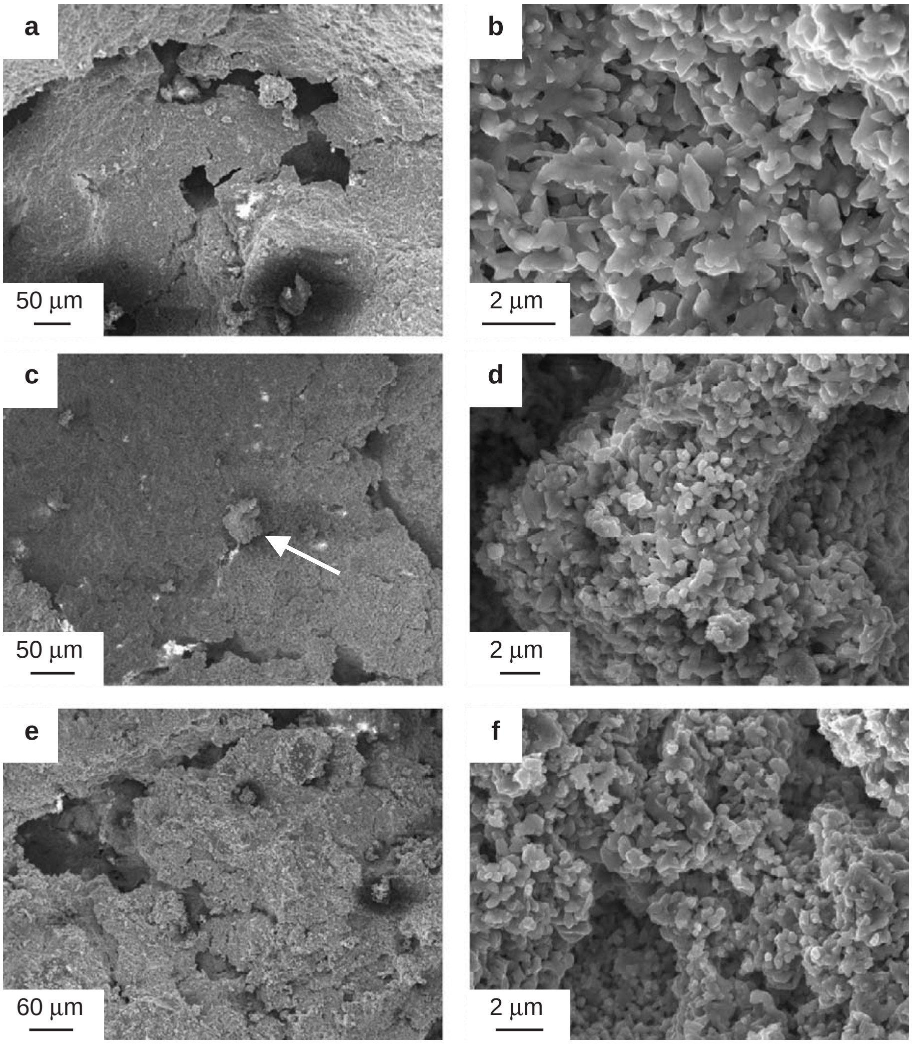

Fig. 10. SEM secondary electron microphotographs of LA mortars after 4 days of forced carbonation (a and b), LP mortars at 8 days of forced carbonation (c and d) and LPA mortars at the end of the carbonation test (e and f).

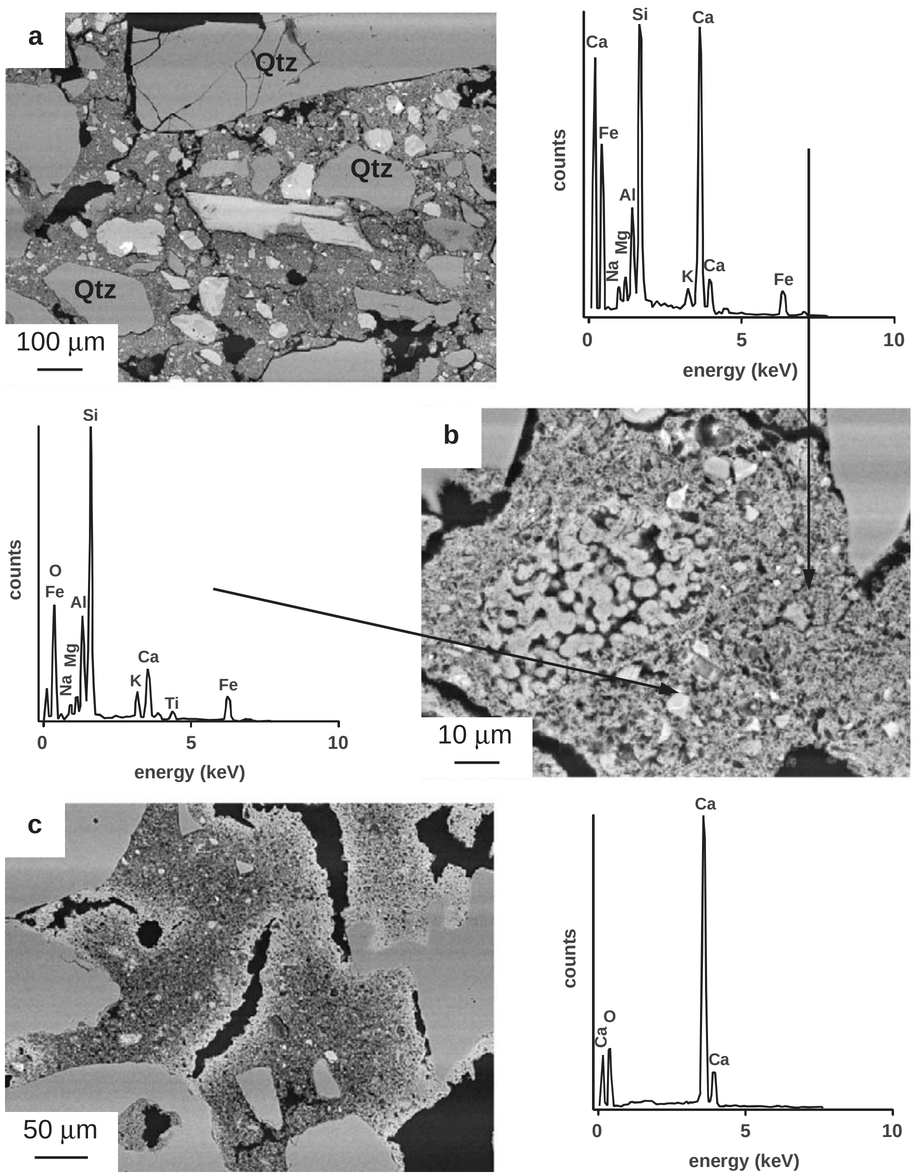

Fig. 11. BSE images and EDX analyses of mortar samples: (a) general aspect of LP mortar (Qtz=quartz); (b) detail of the surface of the aggregate; EDX analyses show its composition and that of pozzolana particles; (c) aspect of advanced carbonation along fissures in L mortar.

sections portlandite crystals could not be distinguished from calcite crystals as they measured less than 1 μm (Figs. 9 and 10). On the other hand, through microanalysis it was possible to identify the volcanic ash particles (in white). Fig. 11c shows an advanced state of mortar carbonation in the fissures in the mortars, as they facilitate the entrance of CO_2 into the samples.

4. Conclusions

The following conclusions can be reached:

1) Different techniques, such as the determination of the weight of the mortars or the quantification by XRD of the different mineral phases that constitute them, provide very similar results. They enable the speed of mortar carbonation to be calculated and ensure that the process is completed quickly and reliably.
2) In the mortars studied in this work, a ≥90 wt.% portlandite–calcite transformation was achieved by XRD in just over 1 week by subjecting the mortars to a CO_2-rich atmosphere.
3) The carbonation process was not affected by additives, such as pozzolanas or air-entraining agents.
4) Once carbonate formation has reached a level of 90%, the process diminishes sharply. This may well be due to the great heat generated during the portlandite→calcite reaction sufficient to evaporate capillary water, and/or the temperature defined in our research which can diminish the CO_2 solubility, and/or the pore size reduction because of calcite crystallization.

5) Carbonation under natural environmental conditions, besides being a lot slower, cannot reach the same carbonation volume as that achieved by forced carbonation. The importance of CO_2 concentration in the portlandite→calcite velocity reaction has been demonstrated under levels of relative humidity (50%) and temperature (25 °C) programmed specifically for this research. The reaction rate appears to be independent of CO_2 concentration and mostly depends on the reactivity of the lime and the water content.
6) Pores are round when an air-entraining agent is added to the mortars. Furthermore, the addition of air-entraining agents to the mortars helps to eliminate or at least to diminish significantly the retraction of fissures that develop, albeit in very small amounts, in the other groups of mortars. This additive does not increase the carbonation rate of lime mortars because of the low degree of interconnection between pores.
7) We demonstrated the existence of the lime–pozzolana reaction, although the quantity of calcium-silicate phases developed was too small to be detected by XRD. This is probably due to the fast carbonation of lime mortars which can destroy the microstructure of these new mineral phases. Specific analyses (FESEM-INCA) were required to confirm that these new calcium silicates had indeed been generated.

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