



Crystal development during carbonation of lime-based mortars in different environmental conditions



Duygu Ergenç*, Luz S. Gómez-Villalba, Rafael Fort

Institute of Geosciences IGEO (CSIC/UCM), c/Doctor Severo Ochoa, 7, 28040, Madrid, Spain

ARTICLE INFO

Keywords:

Climatic chamber
Roman ceramic aggregate
Calcite
Aragonite
Vaterite

ABSTRACT

This study examines crystal development during the carbonation of lime mortars according to the additives used and curing conditions. Two types of samples were prepared, one with sand and the other one additionally including Roman ceramics. These mortars were cured: 1) by spraying with a carbonation accelerator product under laboratory conditions; 2) in a climate chamber under 20 °C, 60% relative humidity, and 1600 ppm CO₂; and 3) under laboratory conditions as controls. Polarized light microscopy, SEM-EDS and XRD were used at 28, 90, 120 and 180 days to monitor the carbonation process. Observations indicate the development of different CaCO₃ polymorphs, which appeared as metastable phases. The early nucleation of a well-defined calcite phase as the most stable CaCO₃ polymorph was only identified in the chamber-cured samples. Differences in the pore network were observed depending on the composition and morphology of the mortar components and the environmental curing conditions.

1. Introduction

Lime has been long used as one of the main components of mortar and has a long-standing history of use as a construction material. Lime-based Roman mortars show excellent properties, determining their persistence for two millennia attributable to a high quality manufacturing process. In effect this durability is still detectable in archaeological sites today.

Interest in the use of lime has been rekindled and today it is being ever more used as a repair material in the restoration and conservation of cultural heritage buildings mainly because it is compatible with authentic building materials and is more sustainable than cement.

To manufacture lime mortar, limestone fragments are burned to yield quicklime (CaO), which when hydrated with an excess of water generates slaked lime (Ca(OH)₂). Over time, this slaked lime hardens with atmospheric CO₂ producing carbonates and ending the cycle with the nucleation of a re-formed CaCO₃. However, in the carbonation process, a series of reactions may occur, which may be conditioned by several environmental variables such as relative humidity (RH), pH, temperature, and atmospheric CO₂ concentration. In turn, the characteristics of each of the constituents used to prepare the mortar may affect each reaction step. For instance, the morphology and quantities of additives and aggregates used to prepare a mortar will affect the final microstructure of the product.

Several studies have focused on historic [1–4] and repair mortars

[5–8]. As various factors affect the final performance of a mortar, there have been numerous lines of research. The mortar binders examined so far have been those comprised of pure limestones or dolomitic limestones [9,10] or in the form of quicklime [11], lime putty [12], or hydrated lime powder [13]. Some authors have assessed different aggregate proportions [14–16], or additives such as vegetal and wood fibres [17], water repellent agents [18], or natural and artificial pozzolanic additives [19–23]. Many studies have examined the effects of different factors on the carbonation reaction [24–29].

Among the different properties analysed, porosity is an important factor for the performance of a mortar in terms of mechanical strength and hydric behaviour. Grain size distribution and entrapped air during manufacturing are the main porosity determinants [30]. However, during hardening of mortar, both the pore network and pore size distribution change [31]. Mortar carbonation and porosity are inversely related. Thus, the greater the carbonation of a mortar, the lower its porosity, while a reduced porosity will prevent CO₂ accessing the mortar and therefore hinder the carbonation process. However, not always will all new carbonated phases be beneficial and porosity will also depend on the type of nucleated polymorph involved. Although carbonation basically involves the transformation of portlandite, Ca(OH)₂, into calcite, CaCO₃, the process is much more complicated than this and stable calcium carbonate will not always be precipitated. In addition, the porous medium will also be defined by the stability, shape, and particle size of the different polymorphs of CaCO₃ in the

* Corresponding author.

E-mail addresses: duyguerg@ucm.es (D. Ergenç), luzgomez@geo.ucm.es (L.S. Gómez-Villalba), rafael.fort@csic.es (R. Fort).

mortar.

The crystal dynamics of lime-based mortar has been described as the transformation of platelike or hexagonal portlandite crystals [32,33] into scalenohedral- and rosette shaped calcite crystals upon ageing [26]. In addition, according to some authors, scalenohedral crystals arise from amorphous CaCO_3 forms as a result of dissolution re-precipitation phenomena when there is Ca^{2+} ion excess in a CO_2 rich environment [25,26,34].

The carbonation model of Van Balen and Van Gemert [35] explains the carbonation rate as essentially dependent on the diffusion of carbon dioxide and its reaction with water. This model also indicates that the environmental conditions of the carbonation process and interactions among the lime, aggregates and additives have a direct impact on different crystal habits and their stability.

The state of the lime determines the chemical reaction between aggregate and binder. For instance, aged lime putty has randomly oriented nanoparticles and therefore a higher reactivity than dry hydrated lime [32,36]. Also, a greater specific surface area of lime putty increases the speed of the reaction independently of the amount of CO_2 [24]. Temperature, RH, pH and CO_2 diffusion are the environmental factors that play the more important roles.

According to Çizer et al. [27], under conditions of high RH and CO_2 and continuous dissolution and precipitation, portlandite is replaced by calcite pseudomorphs and the calcite crystal habit changes. In addition, the time period during which the mortar is exposed to CO_2 affects the carbonation depth. However, not only in conditions of high RH, will the CaCO_3 polymorphs be nucleated. Indeed, when RH is low, amorphous calcium carbonate appears as the first stage of the carbonation process, and this is followed by the formation of metastable or unstable phases [37].

To gain further insight into crystal growth in lime-based mortars, the present study compares crystal development in lime mortars with and without ceramic aggregates during their carbonation in different curing conditions.

2. Materials and Methods

2.1. Mortar Sample Preparation

Two mortar mixtures were prepared: one containing calcite lime putty and siliceous sand (M1) and the other containing the same ingredients plus an aggregate composed of ceramic dust and fragments replacing some of the sand (M2). These formulations and aggregate grain size distributions were based on data obtained for Roman mortars of the Complutum archaeological site (Alcalá de Henares, Spain) [38]. To prepare the mortar mixtures, lime putty, standard siliceous sand [39] and ceramics were used. The latter were Roman ceramics collected from the Complutum archaeological site that had been previously crushed and sieved according to the grain size of the mortar at the site (Fig. 1). In M2, grains larger than 2 mm were ceramic fragments and there was a higher percentage of fines ($< 125 \mu\text{m}$) due to the ceramic dust (Fig. 1). The sand grains showed a rounded to angular morphology whereas the ceramics had angular to very angular forms.

The binder-aggregate ratios used by volume were 1:3 (lime: sand) for M1 and 1:0.5:1:2 (lime: ceramic dust: ceramic fragments: sand) for M2. Although the lime paste had a 85% water ratio to ensure suitable workability extra kneading water was required during mixing. Less than half the volume of the binder was added to the M1 mix and half this volume was added to the M2 mix which resulted in 120 mm and 130 mm flow table diameters, respectively.

Samples of the two mortar types were prepared and used to fill metal prism moulds of dimensions $160 \times 40 \times 40$ mm ensuring adequate workability according to guidelines for test mortars EN 1015-12 [40]. Fifteen days later, the samples were demoulded and left in an open chamber under conditions of controlled temperature (T) $25 \pm 3^\circ\text{C}$, relative humidity (RH) $34 \pm 8\%$ and carbon dioxide (CO_2)

703 ± 116 ppm (Table 1).

The two manufactured mortars M1 and M2 were each divided into three, and each portion cured in three different ways for 180 days: Treatment A + L, specimens were sprayed with the carbonation accelerator DiloCarB®, a commercial product (diethyl carbonate dissolved in ethanol and water) used to enhance carbonation reactions [41]; Treatment C, specimens were placed in a climate chamber under controlled conditions of temperature (20°C), relative humidity (60%) and CO_2 concentration (1600 ppm); and Treatment L, specimens were left to cure under laboratory conditions as controls [38].

2.2. Experimental Procedures

At each of four curing ages (0–28 days, 28–90 days, 90–120 days and 120–180 days), all six mortar blocks (three M1 and three M2) were characterized by X-ray diffraction (XRD) and scanning electron microscopy (SEM) with energy dispersive X-ray spectroscopy (EDS).

For the comparative analysis, samples were taken from the same place in each block. A 1 cm-thick slice was cut 4 cm from one edge of the block and this portion was divided into two: one for thin section preparation for polarized light microscopy (PLM), and the other for both SEM-EDS and XRD (Fig. 2).

Polished thin sections were examined by PLM using an Olympus BX51 instrument equipped with a digital camera Olympus DP12 to capture images. Quantitative porosity was measured on these sections by image analysis using Image J and Photoshop CS10 software. XRD diffractograms were obtained on powder particles (sieved $< 50 \mu\text{m}$) using a Bruker D8 Advance X-ray diffractometer fitted with a copper anode tube and graphite monochromator and equipped with PC-ADP diffraction software. XRD patterns were acquired in operating conditions of 40 kV and 30 mA at 2θ angles of $2\text{--}68^\circ$ with a 0.020 -step scan at a speed of 2° per minute. Data were analysed using the databases RRUFF (Raman spectra, XRD and chemistry data for minerals) and JCPDS (Joint Committee on Powder Diffraction Standards).

For SEM-EDS, pieces of mortar were gold-coated and examined in a JEOL JSM 6400 scanning electron microscope fitted with an Oxford-Link Pentafet energy dispersive X-ray microanalyser.

3. Results and Discussion

3.1. Mineralogical and Petrographic Properties

Observations on the thin sections of the M1 mortar revealed mainly quartz and feldspar sand grains along with opaque minerals embedded in the micritic calcite ($< 4 \mu\text{m}$) lime binder. Under plane polarized light, the M2 thin sections showed a different appearance due to the presence also of ceramic dust and fragments. In these samples, binder and aggregates appeared more attached to each other.

During the curing process, the porosity of the mortar tends to decrease. This can be mainly attributed to the volume increase produced after the transformation of $\text{Ca}(\text{OH})_2$ into CaCO_3 crystals. Pore morphology may also vary. Effectively, fracture porosity dominates and is frequently observed as fissures at pore boundaries joining together through drying-induced shrinkage.

To examine the relationship between porosity and a changing microstructure, microscopy is the most suitable technique [42]. Hence, the main objective of petrographic observation was to identify modifications produced in the crack-pore networks during carbonation.

Using this technique, the porosity calculated by image analysis for the chamber-cured M1C samples was 32.39% at 28 days and 10.74% at 180 days, meaning a reduction of 66.8% (Fig. 3). For the M1A + L samples, porosities fell by 50.5% from 36.29% at 28 days to 17.95% at 180 days (Fig. 4). The larger shrinkage cracks formed in the drying/hardening period in these samples were clearly filled after carbonation. The lowest porosity reduction of 24.2% (33.27% to 25.23%) was detected for the M1 mortars cured in laboratory conditions (Fig. 5).

Download English Version:

<https://daneshyari.com/en/article/7969037>

Download Persian Version:

<https://daneshyari.com/article/7969037>

[Daneshyari.com](https://daneshyari.com)