Construction and Building Materials 148 (2017) 38–48

Contents lists available at ScienceDirect

Construction and Building Materials

journal homepage: www.elsevier.com/locate/conbuildmat

Experimental analysis of the carbonation and humidity diffusion processes in aerial lime mortar

Mateus A. Oliveira [a], Miguel Azenha [a,*], Paulo B. Lourenço [a], Anna Meneghini [a], Erika T. Guimarães [a], Fernando Castro [b], Delfim Soares [b]

[a] ISISE – Institute for Sustainability and Innovation in Structural Engineering, University of Minho, School of Engineering, Department of Civil Engineering, Campus de Azurém, 4800 Guimarães, Portugal
[b] University of Minho, School of Engineering, Department of Mechanical Engineering, Campus de Azurém, 4800 Guimarães, Portugal

HIGHLIGHTS

- Pioneering measurement of humidity diffusion in lime mortars.
- Effect of specimen size on carbonation progression dependent on age of exposure.
- Study of carbonation through TGA testing up to the decarboxylation range.
- Differences observed between direct/indirect estimation of carbonation through TGA.
- Maximum degree of carbonation of ~70% in the studied mortar.

ARTICLE INFO

Article history:
Received 28 July 2016
Received in revised form 11 April 2017
Accepted 14 April 2017
Available online 10 May 2017

Keywords:
Aerial lime
Mortar
Carbonation
Thermogravimetric analysis
Humidity diffusion process
Phenolphthalein
Compressive strength

ABSTRACT

Aerial lime has been commonly used as binder for preparing mortar in masonry constructions for centuries. Knowledge about the material behaviour of aerial lime is however still limited, and contributions are necessary for better understanding of the evolution of its physical and mechanical properties, in particular concerning the structural behaviour of both historical and new constructions comprising of aerial lime. In this work, an experimental program was developed in order to study aerial lime mortars, specifically addressing the drying and carbonation processes. Regarding the measurement of drying process, the humidity diffusion was monitored in one-dimensional flux conditions. The phenomena associated with self-desiccation were also investigated. For evaluation of the carbonation process, different cylindrical specimens have been studied with phenolphthalein indicator and thermogravimetric analyses. In order to exclusively investigate the carbonation reaction, without the effect of internal humidity gradients in the tested specimens, thin discs of mortar were tested. Also, the compressive strength evolution was analysed using cubic specimens. The most relevant findings can be summarized as following: *(i)* humidity diffusion was quicker than normally observed in cement-based materials; *(ii)* a strong effect of the size of specimens has been observed in early ages (before 10 days), which became negligible as time progressed; *(iii)* up to 70% maximum carbonation was observed in TGA testing, when direct measurement of actual decarboxylation was made, as opposed to mere inference based on the dehydroxylation.

1. Introduction

The structural safety of historic buildings that compose cultural, artistic and architectural heritage is a rather relevant issue [1,2]. Indeed, the preservation of historical constructions is of major importance for society and for future generations [1]. A detailed structural analysis of ancient masonry structures demands careful consideration of mortar proprieties [1,3]. In fact, even though mortar only corresponds to approximately 15% of volume of masonry structural elements [4], it has been acknowledged as the main component, responsible for structural deformations [5]. As it has widely been used as binder in ancient buildings throughout Europe and Middle-East, the study of lime based mortar has great importance [6–8].

* Corresponding author.
E-mail address: miguel.azenha@civil.uminho.pt (M. Azenha).

http://dx.doi.org/10.1016/j.conbuildmat.2017.04.120
0950-0618/

In this way, a relevant slice of the contemporary interests in aerial lime is related to the context of restoration and preservation of historical heritages [1,2,8,9]. Aerial lime is basically composed by CaO and, in some cases, it may present significant content of MgO as well [10,11]. This work concerns a type mainly composed by CaO. Through hydration of lime, calcium hydroxide – $Ca(OH)_2$ – is obtained, which is then able to harden when exposed to atmospheric CO_2. This process is known as carbonation [1,6,9,10,12,13] and acts progressively towards the inner regions of the material [7], as carbon dioxide is able to diffuse through it, details are given by Cizer [13]. However, before carbonation takes place, an initial drying process is verified on lime-based mortars, resulting in eventual drying shrinkage [14], which may cause surface cracks. In general terms, carbonation is influenced by the surrounding environment and characteristics of the material [8,9]. Details of influence of aggregates on carbonation can be seen in the work of Arizzi and Cultrone [8]. Several environmental parameters are known to influence the carbonation process, namely temperature, relative humidity and carbon dioxide concentration [15–21]. The mixture composition also plays a key role in the evolution of carbonation, by influencing the porous matrix characteristics and subsequently affecting the depth of the carbonation front [8,9,22].

In aerial lime mortar, carbonation has very important structural consequences due to the direct effect on physical and mechanical properties. In general, carbonation causes an increase of density and strength, while progressively modifying the pore structure of the mortar. This process may take decades or even centuries in thick elements [6,8,9,12]. Thereby, the conversion of calcium hydroxide into carbonate is often characterized as a long-term process [6,23]. In addition, as $CaCO_3$ crystals precipitate, the size of pores is reduced, thus hampering the accessibility of CO_2 to inner regions of the material [6,10,22].

Carbonation has been experimentally evaluated in diverse ways by several authors [6,8,9,12]. The thermogravimetric analysis, X-ray diffraction and the thermal differential analysis can measure the content of $CaCO_3$ [24,25] and are well-known quantitative methods for such purpose. Other methods for carbonation evaluation are cited in literature, namely the phenolphthalein indicator, scanning electron microscopy, optical microscopy and Raman spectroscopy [26–29], among others. Focus is now given to the techniques adopted in the scope of the present research: Thermogravimetric analyses (TGA) [1,6] and phenolphthalein [1,6].

In thermogravimetric analysis (TGA), a material sample is submitted to a defined rate of temperature change until a maximum value is reached [30–32]. The mass of the sample is monitored through the temperature range, and graphic results are provided by means of a weigh *vs.* temperature curve – TGA curve [30–33]. This method is frequently used in the characterization of various types of materials [1,6]. Particularly for aerial lime mortar, this technique is useful to investigate two phenomena that provide information regarding the reactants/products of the carbonation process: dehydroxylation and decarboxylation [1,30,34]. Phenolphthalein is a recognized method to study the carbonation in different materials [1,6]. Even though phenolphthalein is known to be relative, it allows comparative evaluations between specimens. That was the reason for its adoption in parts of this research when comparative studies were in order, and the TGA testing equipment was not available.

With regard to the drying process, even though several authors have already measured humidity diffusion in cement-based materials [35–38], no literature reference could be found in concern to aerial lime mortars.

The humidity affects different properties of the mortar, such as mechanical behaviour [1,6], carbonation and other phenomena. The average pore relative humidity (h) and the state of water itself in the pore network (liquid/gaseous) also affect the diffusion of CO_2 through the mortar. Indeed, it has been reported that the diffusion in a liquid is about 10.000 times slower than in air [6,17].

In terms of experimental testing, mechanical properties of lime mortar were studied by different authors [6,39–41]. For instance, the effects of the composition were studied by Arizzi *et al.* [8] and Lawrence [6], and the influence of other aspects such aggregates type by Lanas and Alvarez-Galindo [42]. Despotou *et al.* [43] presents a summary of diverse studies about the carbonation process in aerial lime mortar, describing and summarizing the results of different authors, with experimental work.

Based on the presented literature review, it has been demonstrated that the evolution of mechanical properties of aerial lime mortars are related with drying and carbonation processes [44], which are in turn coupled with together.

The strategy adopted in this work intends to investigate humidity diffusion, carbonation process and the influence of both phenomena on the mechanical properties of aerial lime mortar. The experimental program started with a pioneering experimental assessment of internal humidity distribution with embedded humidity probes.

Following which, the effect of specimen size on the carbonation front was investigated with phenolphthalein indicator, so as to infer potential effects and attempt to relate them with findings obtained from humidity profiling.

Further tests were performed to assess carbonation behaviour, while trying to minimize the effects of internal moisture gradients in the mortar, with experiments performed on small 8 mm thick discs. The extent of carbonation was assessed through TGA, with direct measurements taken in the decarboxylation range. Discussions of potential distinct interpretations have been carried out, by comparing results with those that would be inferred with basis on measurements taken at the dehydroxilation range combined with stoichiometric considerations. In the end, as a consequence of drying and carbonation processes, the evolution of compressive strength over time was investigated.

2. Components, mixture and specimens preparation

2.1. Lime

Micronized quicklime was adopted as binder in the present work. Lime was provided by the company Lusical, S.A. from the Lhoist group [45] and classified as CL90 Q [46], which means that the percentage of CaO + MgO should be over 90% in terms of weight. To characterize the material and also to attest this condition, the material was analysed by X-ray Fluorescence Spectroscopy – XRF.

In all the performed analyses, the apparatus used to perform the analyses was a TGA model 2960 SDT V3.0F from TA Instruments [47,48]. The equipment can perform simultaneous DTA and TGA testing by measuring both the heat effects (DTA) and weight changes of the sample [47,49].

The TGA test was done with temperature ranging from 20 to 1100 °C, under an inert Argon atmosphere, obtained with a constant flow of 100 mL/h of Argon, at a rate of 10 °C/min.

In thermogravimetric analysis of lime and lime mortars, each constituent has its own temperature range of decomposition and a specific mass loss, depending on the stoichiometry of the involved decomposition reactions. For instance, calcium hydroxide decomposes through a process termed as dehydroxylation, which typically occurs in the range 300–550 °C [6,12]. The decomposition of calcium carbonate, termed decarboxylation, occurs in the range 650–950 °C [6,12].