



Evolution of mechanical properties in aerial lime mortars of traditional manufacturing, the relationship between putty and powder lime

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HIGHLIGHTS

- The variations in binder/water ratio can have a counterproductive effect on the mortar carbonation process.
- The carbonation velocity in lime mortar is not related to the type of lime. The carbonation process slows down in most mortars at 90 days.
- The flexural and compression resistance of traditional lime mortars increases gradually and in relatively short periods of time (around 90 days).
- The type of Liesegang patterns observed in the lime mortar is directly related to the characteristics of the carbonation process of binder.
- SPL mortars have a higher volume of macropores than CL mortars that are characterized by a higher microporosity.

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ABSTRACT

In recent years, numerous studies have been published on the technology of industrial aerial lime mortars. These papers refer to the incidence of carbonation process and mechanical behavior in its properties as construction material, of interest for its application in Cultural Heritage conservation. Among other issues, the importance of the type of aggregate (composition and granulometry) and relation binder/water (B/W) in its properties are highlighted. There are fewer papers in which the type of lime is about, especially on the basis of its manufacturing process (traditional or industrial), on the presentation of the product (powder or putty), or referred to the different types of mortars (prepared in situ or pre-dosed). In this paper, the behavior of aerial lime mortars elaborated with traditional lime has been determined and a comparative study has been carried out with pre-dosed mortars of powder (mCL) and in putty (mSPL) lime for its application in render mortar (B) and plaster mortar (F). The control parameters have been mechanical resistances-elasticity, ultrasound velocity, carbonation process and distribution pore size and surface area by mercury porosimetry. It is concluded that the behavior of traditional lime mortars, both in putty and powder, depends on the B/W ratio, the type of aggregates and the lime content. The importance of the application of the product in the building as the behavior of the mortar is very sensitive to kneading water content it shows; aspects that define the plasticity of the mortar. It is also concluded that the carbonation of traditional lime mortars is not slow and that, under optimal dosages conditions, can be finished before 90 days. It is also verified that a higher carbonation rate does not imply better properties of the mortar in its long-term construction. The utility of ultrasound velocity test as a non-destructive test and easy to apply on building for the quality control of traditional lime mortars and its consistence values it highlights, as is a macroscopic property of easy control during the elaboration of the product.

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1. Introduction

At present, the quality control of lime mortars is of maximum interest for its application in the Cultural Heritage conservation.

In this sense, the concept of compatibility of the restoration materials with the archaeological and historical materials is questioned from the Venice Charter (1964); where this criterion of application is highlighted, although the technical requirements could not be established at that moment due to ignorance about the behavior of the historical materials themselves. For all this, a special interest arises by the study of lime mortars [1] that has given as resulted diverse investigations developed in the last decades. The

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pre-dosed products based on lime are currently on the market, and the responsible of archaeological and historic buildings conservation continue to question their behavior on building, what is preventing these products from entering the market with suitable quality control.

In this paper, pre-dosed mortars are studied, elaborated with traditional lime in its two varieties: CL-90 powder lime (hereinafter CL) and CL-90-SPL putty lime (hereinafter SPL). A suitable characterization is the basis for their use Cultural Heritage conservation [2–6] which makes it possible to maintain the value and usefulness of these lime by UNESCO in its list of *Best Practices for the Safeguarding of the Intangible Cultural Heritage of Humanity*, in Bali (Indonesia) in November of 2011 [7].

It is of interest in this paper to highlight the incidence of the type of lime (CL and SPL), both of traditional manufacturing, in the mechanical and elastic properties evolution of the mortars and their relationship with the carbonation process. On the specimens have been determined ultrasound velocity, apparent density, open porosity, mercury porosimetry, granulometry and composition of the aggregates [8–12]. At the same time, a control of the transformations from portlandite to calcite was carried out by means of mineralogical and microtextural analysis methods by X-ray diffraction (XRD), SEM, and increase weight over curing time and phenolphthalein test [4,13].

1.1. Mechanical properties of lime mortars

The physical-mechanical properties of lime mortars, including their deformational behavior under stress [14], are measurable parameters that greatly assess their compatibility with archaeological, historical and traditional construction materials [15] and their durability in service [16]. The investigations carried out in the last 20 years have focused on the use of analysis methods that allow identifying the aspects that most affect their best or worst mechanical behavior, and carbonation has been the most investigated since it is considered most important factor [17–22,9,23,24].

The carbonation process over time of lime mortars depends of the porosity and diffusivity of the CO₂ through the material, as well as of its application on building [18] and in particular of the open porosity [25–27]. Several environmental parameters affect the process such as temperature, relative humidity and concentration of carbon dioxide [28,29]. It is well known that there is a range of RH in a certain temperature interval that favor mortar carbonation process and that, for example, RH above 85% or under 40% slows down or even hinder carbonation [20,30].

On the other hand; the mechanical behavior of lime mortars depends on the characteristics of the raw materials and the elaboration process since these aspects define the porosity spectrum of the mortar. The type of lime [17], amount of kneading water, composition and granulometry of the aggregates [19] have an important role. For example limestone aggregates produce pores of large and medium radius that allow the greatest carbonation, reducing stress during drying and crystallization damage [22]. The binder/water ratio also has a significant impact on the porosity of lime mortars; most of the pores in the putty lime are in the range of 0.5–5 μm, favoring the carbonation process by means of normal diffusion or Flick's diffusion, being the majority of the pores >0.45 μm [10]. This range of pores decreases with the increase in lime content and increases as the kneading water content of the mixture increases. The porosity is reduced as carbonation proceeds in from 0.01 to 0.03 μm ranges [10], being able to pass to Knudsen's diffusion; this can cause this process to vary in velocity and intensity over time [9]. The reactivity of the lime and the water content are the aspects that most influence [13].

The relationship between textural characteristics, ultrasound velocity and mechanical properties in the lime mortars has been

revealed in a large number of papers [8,4,31] and is currently considered of great interest in the characterization of these materials. The ultrasound velocity (non-destructive technique) is characterized because an increase in the velocity of the ultrasonic waves indicates a greater degree of compactness and lower anisotropy [8,31,32]. The ultrasound velocity depends of the porosity and type of aggregates (composition, granulometric distribution); however its evolution over time indicates modifications in the microtexture that affect mainly the binder [4] so it is of great interest for the characterization of mortars with different types of lime.

1.2. Carbonation process

Currently is of great interest to understand how carbonation evolves in the lime mortars and with it the mechanism of the quasi periodic precipitation of calcium carbonate. The drying of mortars plays an important role in the carbonation process. During the drying phase of lime mortars, cracks can be generated that can increase porosity, but after this period the general tendency is to increase their density and reduce their porosity [4,36,29] due to the filling of the pores by precipitation of calcium carbonate. The transformation from portlandite to calcite takes place according to the following mechanisms: diffusion of gaseous CO₂ through the open pores, dissolution of Ca(OH)₂ in the water and release of Ca²⁺ and OH⁻ ions, absorption and dissolution of CO₂ in water, carbonic acid (H₂CO₃) formation, reaction between Ca²⁺ and CO₃²⁻, nucleation of CaCO₃ and finally crystalline growth [13,17,18,20,21,33–35]. In these processes the type of lime must have an important role.

The crystallization process takes place by replacement; the mechanism is by precipitation-dissolution. The new mineral phase is formed by precipitation and the effect of the pressure generated is responsible of the dissolution of the initial phase, these processes take place simultaneously [37]. The size of the portlandite crystals seems to have an impact on the transformation to calcite, since the smaller crystals have a larger surface area and the CO₂ will access more quickly [38]. Previous studies indicate that in conditions of very high supersaturation and high nucleation velocity (favored by the small size of the pores generated by limes), the formation of colloidal microcrystalline or monohydrocalcite calcite [21,39] or even amorphous takes place [40]. The calcium carbonate, which appears as an amorphous (ACC) in the form of spheres smaller than one micron, becomes calcite as the reaction progresses [41]. The calcium carbonate pseudomorphs preserve the external shape of the portlandite crystals [42,43] and grow epitaxial on their surface [0001] following a crystalline orientation [20,44], by preventing the entry of CO₂ to the inside of the mortar. Later, as a result of the Ostwald maturation, the size of the colloid (or amorphous) of the calcite or precursors is transformed, forming bands of larger and malleable calcite crystals. This ring or band arrangement would explain the Liesegang patterns observed in lime mortars [32,36]. On the other hand a small advance of the carbonation takes place in the core of the mortar ahead of carbonation front, at a velocity that is probably related to the distribution of the pore size of the mortar [36]. Therefore, the formation of these ring or band has been related to the instability of the Ostwald maturation process, linked to the supersaturation of pore size smaller than 0.1 μm and high nucleation rates [21].

Several responsible parameters of the spatial geometry and the time relations shown by the Liesegang patterns have been established. The initial concentrations of reactants, the surface of the reaction front, the geometry shape, volume, type of the reactant and viscosity. There are other external parameters that influence as temperature, pH and the presence of impurities among others [45]. For these reasons it has been the object of this paper to observe the development of these ring or band in the mortars

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