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A new methodology to recognize the use of long aged lime putties

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ABSTRACT

In this paper a new methodology, combining chemical and thermogravimetric (TG) investigations, is proposed useful to get information about the use of lime putties after long aging. The method is applied with reference to two Roman mortars with different age: I C AD, when the technology of aging lime putty in deep ground hollows under a thin water layer for long times was fully assessed, and II C BC, when the Roman hydraulic mortars technology was in its infancy.

The amounts of binder phase were estimated from the residue of HCl attack; a simple method was followed to assess the length of the chemical attack. The composition of the binder phase (as calcite and hydraulic components contents) were estimated from the TG curves. By combining the above results, the structurally bound water contents in the hydraulic components could be estimated.

With respect to the II C BC mortar, the I C AD one shows: a) much greater structurally bound water content; b) an earlier CO_2 removal during a TG run. These differences are explained on the basis of the use of differently aged lime putties, in good agreement with the expectations based on the mortars dating.

1. Introduction

Mortar characterization plays an important role in the study of the historical buildings and associated structures; these studies are [1–3] relevant not only for identifying the source of materials employed in historical edifices but also to get information on the applied technology in view of conservation proposals. It is known that failure of modern mortars currently employed in restoration procedures of ancient buildings is mainly due to the ancient mortars different nature and production technology, e.g., calcareous rocks firing temperature, lime slaking, grain size distribution, binder/aggregate ratio etc. [4]. In this context, the investigation into the traditional production technology of mortars and plasters is of great significance to allow an effective conservation of mortar [4].

The analysis and characterization of old mortars is performed by many researchers. Various methods and tools have been proposed, during the last decades, focusing on the physical, mineralogical, chemical and mechanical properties of mortars [5,6]. In particular Thermal Analysis Techniques are largely used to detect hydraulic compounds and to identify the type of mortar [7–9]. Thermogravimetry is particularly useful to assess the amount of mineralogical phases present. Its use has been proposed also to study hydration kinetics of cement pastes [10,11]. It was shown, in fact, that the chemically bound water amount evaluated using thermogravimetric analysis is proportional to heat of hydration and can be used as a measure of hydration.

This paper sets up a new methodology that (for the first time to the knowledge of the authors) combines chemical and thermogravimetric measurements to evaluate the structurally bound water contents in the hydraulic components of the mortars; furthermore (for the first time to the best of our knowledge) it is shown that this bound water content determination can be combined with the occurrence of earlier CO_2 removal during thermogravimetric run, to assess the use of lime putties after aging in deep ground hollows under a thin water layer for long times. This is an important mortars technology aspect: slaked lime aging under a thin water layer for, also, several years is well known to greatly affect the mortars structure and performances.

The methodology is described and discussed with reference to two Roman mortars. The former is dated to I C AD when, following Vitruvius (end of I C BC) and Pliny (I C AD), the technology of lime putty aging was fully assessed, as better reminded below. Whereas the latter is dated two centuries back (II C BC) when, as better reminded below, the Roman hydraulic mortars technology was in its infancy.

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It's well known that Roman mortars have long attracted the attention of many researchers in an attempt to discover the "secrets" of their extraordinary durability [2]. One of these "secrets" is the use of mixtures of lime and pozzolan that dominated in constructions [2,12] during Roman period (2nd C BC-3rd C AD). In fact Vitruvius, in his book "De Architectura" written at the end of I C BC, and Pliny, in his book "Naturalis Hystoria" written in the I C AD, gave the rules to make resistant constructions [13]. Romans knew that the use of pozzolan, as an aggregate in hydrated lime mixture, greatly improved the mechanical properties and durability of the resulting mortars [2,13]. Another "secret" may be considered the use of long aged lime putties. In fact lime putty storage under water for a long period of time is recognized to improve the quality of lime mortars and plasters [14]: aged lime putty assures plasticity, workability and water retention necessary for preparing a durable and high quality mortar or plaster. It is known that [13] at the end of IC BC Romans largely used lime which had been aged in deep ground hollows under a thin water layer for long periods. In fact Pliny the Elder(I C AD) [13,15] reports that the builders of Rome were advised to use fat lime only after it had been left slaking for at least three years. Pliny the Elder reports [13,15] on lime slaking as follows: "It is also a fact that the 'calx intrita' (mixture of lime and water) improves with keeping; in the old building laws is to be found a regulation that no contractor is to use a "calx intrita" that is less than three years old; consequently, old plaster work was never disfigured by cracks". However already at the end of I C BC Vitruvius [13,16], in his book "De Architectura", advised that the lime was to be slaked during a long time to allow nonfully-calcined limestone lumps to hydrate and acquire a fine, homogeneous consistency. Recent investigation on lime putty [14] showed that, during long slaking, portlandite ($Ca(OH)_2$) crystals undergo both an important size reduction and a significant morphological change giving, finally, submicrometer, platelike crystals.

Herein we propose a procedure that, combining chemical and thermogravimetric techniques, allows to assess the use of long aged lime putties. The methodology is described and discussed with reference to two Roman mortars of different age, II C BC and beginning of I C AD, the second one being expected to have been prepared with long aged lime putty. Both mortars come from Pozzuoli (Puteoli in Roman time) that was in the center of the area where pozzolan was extracted. It's worth reminding also that Puteoli was founded by Romans in 194 BC. The town had a rapid development thanks to its harbour that was the most important one of Roman Republic and Empire till I century AD when Ostia harbour (near Rome) took the primacy. It was therefore a town rich enough to host the most skilled workers. Therefore it's highly plausible that the studied later mortar (I C AD) was made with long aged lime putty. The older mortar, instead, is dated two centuries back (II C BC) when the Roman hydraulic mortars technology was in its infancy [12,17]. The paper shows that the proposed investigation leads to results in full agreement with the expectations about the use of long aged lime putties.

2. Experimental

Two Roman mortars have been studied. They are dated II C BC and beginning of I C AD, respectively. In the following they will be distinguished as mortars A (the more ancient one) and B.

X-ray (Cu-Kα) powder diffractometry (XRD) was performed using a Philips Diffractometer model PW1710, with a scan speed of 1° min^{-1}. Crystalline phases were identified, using a built-in computer search program, by comparison with JCPDS cards (International Center for Diffraction Data).

The two mortars were submitted to chemical investigation by exposing 1.00 g of them, for different times (1 h, 3 h, 24 h), to

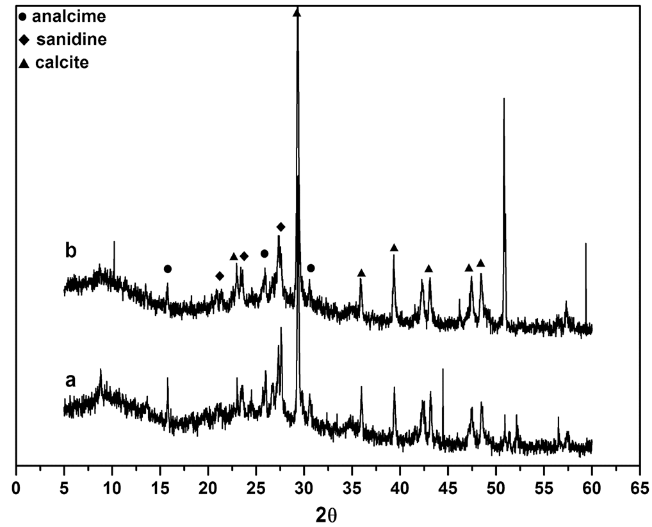

Fig. 1. XRD spectra of mortars A (a) and B (b).

25 ml of concentrated grade (37%) hydrochloric acid (HCl) solution diluted 1:10 and 1:20. Finally the solution was filtered. The residue was washed with distilled water, dried and weighed.

Thermogravimetric Analysis (TGA) was performed in nitrogen atmosphere at heating rate 10 °C/min on 30 mg samples by means of Netzsch Thermo-microbalance Apparatus model TG209. The samples submitted to TGA were taken from pieces of mortars weighing approximately 1.00 g, gently crushed into thoroughly mixed powders. Measurements were carried out in triplicate on each mortar. All the mass changes evaluated from TGA curves reported in this paper are the median of the three values obtained from the three thermoanalytical curves.

Fourier Transform Infrared (FTIR) Transmittance spectra were recorded in the 400–4000 cm^{-1} region using a Nicolet 5020 system, equipped with a DTGS KBr (deuterated triglycine sulphate with potassium bromide windows) detector, with a resolution of 2 cm^{-1} and 20 scans. KBr pelletized discs containing 2 mg of sample and 200 mg of KBr were made. The FTIR spectra were elaborated by means of a Mattson software program (FIRST Macros).

3. Results

The XRD spectra of the two mortars are reported in Fig. 1. They are very similar and dominated by a broad band due to the presence of an amorphous phase; the reflections are easily attributed to calcite, sanidine and analcime.

In Fig. 2 the results of the acid attack are reported (for details see experimental). Fig. 2 shows the diagram of the masses (as w%) of the residues collected on the filter as a function of the time of exposure to HCl solution. Four kind of results are reported: mortar A submitted to 1:10 and 1:20 diluted HCl attack; mortar B submitted to 1:10 and 1:20 diluted HCl attack. All data show a"reversed knee" trend: a very rapid mass decrease followed by a successive very slow mass change. However since the interpolated curves largely superimpose they were not shown in Fig. 2, that reports only the not interpolated data. In one case (mortar B exposed to 1:10 diluted solution) also the value after 30′ exposure is reported.

Fig. 3 shows the FTIR spectra of the residues collected after different times (30′, 3 h, 24 h) in one of the experiments (B mortar exposed to 1:10 diluted solution). In the same Figure the FTIR spectrum of the not leached mortar is also reported for the sake of comparison (Fig. 3a). The bands are easily attributed on the basis of previous papers reported in the literature. The band in the 900–1200 cm^{-1} wavenumber range is linked to the asymmetric and