The influence of natural organic materials on the properties of traditional lime-based mortars

Centauro I.[1], Cantisani E.[1*], Grandin C.[2], Salvini A. [3], Vettori S.[1]

[1] CNR Institute for the Conservation and Valorization of Cultural Heritage, via Madonna del Piano, 10, Sesto Fiorentino (Florence) – Italy.

[2] DIDA - Department of Architecture, University of Florence, via della Mattonaia, 14, Florence – Italy.

[3] Department of Chemistry "Ugo Schiff", University of Florence, via della Lastruccia, 3-13, Sesto Fiorentino (Florence) – Italy.

*Corresponding author e.cantisani@icvbc.cnr.it

ABSTRACT

This paper investigates the influence of natural organic materials on the properties of traditional mortars. Mortar specimens produced with two binders (natural hydraulic lime and aged lime putty) with the same sand and three different organic additives (linseed oil, brown sugar and cow's milk, with different percentages) were created. The colour variations (colorimetry), waterproofing behaviour (water capillarity test), permeability (water vapour permeability test), mechanical properties (maximum resistance to compression test), mineralogical composition (X ray diffraction) and optical properties of mortars (transmitted light microscopy, UV fluorescence microscopy) and carbonation using a phenolphthalein indicator, were evaluated after 28 days, 3, 6, and 12 months.

In this paper we highlighted a series of transformations induced by the additives: a strong modification of colorimetric parameters, a general hydrophobic effect of milk and oil not linked to a total occlusion of porosity, a decrease of mechanical parameters in the specimens prepared with hydraulic lime with respect to the specimen without additives, a different distribution and shape of macropores, a different level of carbonation.

The paper also describes the role of the preparation methods in the influence of natural organic materials on the properties of traditional mortars.

Keywords: natural hydraulic lime, aged lime putty, organic additives, traditional mortars, physical properties, mechanical properties, colour variations.

1. INTRODUCTION

Many kinds of materials have been used in masonry mortars over the years. Besides the basic constituents such as the binder, aggregate and water, mortars may also contain additives which improve their workability and/or to improve the strength and durability of the hardened mortar. The use of such additives overcomes the natural drawbacks (due to the composition of the mixtures, quality of binder and aggregate and their relationship) of the traditional mortar constituents (Rattazzi, 2007; Sickels, 1981; Pecchioni et al., 2008).

Although mortars (especially lime-based ones) with organic additives were frequently used in the past, little knowledge of them has survived to modern times, because it is extremely difficult to systematically discriminate between the organic substances in a complex mixture. This is due to their deterioration as well as the complexity in analysing organic materials in a mortar, since they have often been added in very small amounts, which may be under the detection limit of some analytical methods (Rampazzi et al, 2015; Fang et al., 2014). For example, analysing protein additives is difficult and time consuming because of the very small amount of the additive, the aggressive process of the mortar hardening, and the unexpected modifications of the materials due to ageing (Kuckova et al., 2009). Furthermore, two aspects are rarely considered: the crucial role of some additives in the kinetics of the setting and hardening reactions of the mortar and the various mixing ratios between the binder, aggregate and additives. Understanding the historical techniques used in the production of ancient mortars entails consulting a large number of historical sources

and archive documents (Vecchiattini, 2009). The use of organic additives dates back to the Greek and Roman period when linseed oil was normally added to the lime to obtain a product similar to a glue, which was also used for the canalisations (Plinius the Elder, 2000; Vitruvio Pollione, 2002) or fig latex was added to the plasters in order to slow dry the colour or for waterproofing. However, none of the recipes and prescriptions provide exact details on the amount of raw materials used and how to mix and install the mortars. In fact, from ancient times until the prescientific era, the use of many different substances was not simply based on guesswork but of empirical practice (Arcolao, 1998). In addition, both the preparation method and processing times of mixtures determined the different functions of historic mortars and produced large differences in the artefacts. Three different classes of compounds were widely used in ancient mortars: lipids, carbohydrates and proteins. Lipids of both animal and plant origin (fats and oils) were used as additives in the preparation of mortars, in order to make them more hydrophobic and to improve their workability (Nunes et al., 2012; Cechova et al., 2010). The main art and architecture treatises recommended adding drying oil both in the mortar mixture, to increase its plasticity, and in surface finishing, thus giving the wall protection against environmental humidity (Arcolao, 1998). This protective film, however, is less breathable than that obtained using protein additives. Research on the lipid additives used in mortars shows has still not led to a clear understanding the effects of adding oil on the carbonation of lime-based mortars (Grandin and Ventimiglia, 1997; Grandin and Ventimiglia, 1998; Justnes et al., 2004), or on the pozzolanic reaction of the hydraulic lime-based mortars and concretes (Shasavandi et al., 2010). While the effect of the oil on cement mortars, which were unfit for restoration, has often been tested, there are few deep studies on traditional lime mortars (Justnes et al., 2004). The use of simple and complex carbohydrates as additives is especially linked to the production of stuccos or decoration mortars. Generally, the carbohydrates were indirectly introduced in mortar dough, through the use of polysaccharides, disaccharides,

simple sugars and other component mixtures, including plant sap and starch. Water-soluble elements, such sugar and tannin, give the mortar adhesive properties (sugar) and waterproofing properties (tannin) (Arcolao, 1998). In the 19th century, J. Louis Vicat stated that stucco mortars "improved" with sugar and molasses were able to withstand atmospheric agents for hundreds of years, and he attributed this ability to the influence of sugar on the initial solidification of the mortar. Other important studies were carried out on sugar added to lime and cement (Khan and Baradan, 2008; Susilorini, 2010; Susilorini et al., 2010). Other types of carbohydrates as additives for mortars were used in China, where lime had been used for 5000 years, but where there no technologies based on hydraulic lime because of the shortage of hydraulic materials (such as the pozzolan, widely used by the Romans). In order to improve the properties of construction mortars, the Chinese experimented with several compounds of lime and glutinous rice juice, leaf juices, egg white, fish oil or blood (Arcolao and Dal Bo', 2001). The amylopectin content in rice is responsible for the improved performance of mortars. It controls the growth of calcium carbonate, producing a compact microstructure which is probably the reason for the good performance of lime-based mortar, which thus became more resistant (Yang et al., 2010). Protein-based additives in building materials, in particular in stuccos, have been used since the 1st century BC (Sickels, 1981). The Cretans probably worked mortars to create decorative elements with compounds such as animal glues, egg (both the yolk and the white), casein, etc. (Susilorini, 2010). Bankart (1908) refers to traditions in the Middle Ages, also in Britain and in India, regarding the use of protein-based additives to delay the hardening and, simultaneously, to improve the resistance of mortars. Painting traditions also provide evidence of the adhesive action of milk used as a binder, in particular of casein mixed with lime. This protein is insoluble in water, however in basic solutions such as slaked lime, it forms hard and brittle painting films. At the same time, however, casein and lime produce a virtually irreversible binding, which is used as a powerful adhesive (Cennini, 1971). Bovine milk

and its derivatives mixed with lime were once frequently used as glues, with salicylic acid or potash silicate added to prevent the alteration of the milk over time (Forti, 1989). Many historical sources report combinations of more compounds, containing proteins and enzymes, for example casein and fig latex. The latex breaks the peptide bond of the casein. This influences the precipitation and the fluidization of the casein (Arcolao and Dal Bo', 2001). There are several effects that natural proteins have on mortars, because some properties (air entraining, hydrophobicity, setting acceleration, etc.) depend on both the amino acidic sequence and the polypeptide chain shape. They also acted as retarders in concrete because of complex formation with calcium by crosslinking (Arcolao and Dal Bo', 2001; Jasiczak and Zielinski, 2006; Chandra and Aavik, 1987). For example, the hydrophobic effect is due to a dual mechanism: hydrophobization of the surface of the pores (after the relaxation of the protein chains) and the formation of complexes with the calcium ion (Arcolao and Dal Bo', 2001; Jasiczak and Zielinski, 2006; Chandra and Aavik, 1987). Proteins such as casein can also increase the adhesion of a lime-based mortar, thanks to functional groups (mainly -CONH-, -NH_2, -COOH, -OH, etc.) that are able to form strong interactions with the inorganic compounds. This characteristic has led to the use of proteins as additives for the production of stuccos (Arcolao and Dal Bo', 2001). Given that restoration is "simultaneously history and technique" (Vecchiattini, 2009; Ventolà et al., 2011), a thorough understanding of the original mortar technology and the fabrication of appropriate replacement materials are important research goals. This work describes the influence of natural organic additives (linseed oil, brown sugar, cow milk) on the aesthetical, physical and mineralogical characteristics of mortar. This is done through prototyping different types of specimens in relation to the raw materials, the organic materials added, and the preparation techniques.

2. MATERIALS AND METHODS

2.1. Materials

Various types of mortars, with different binders (natural hydraulic lime and aged lime putty) and types of organic additives (linseed oil, brown sugar, cow's milk) were prepared (Figure 1). Binders were selected according to the traditional use, the function of the mortar, and different hardening processes. Only one type of aggregate was used. Also the additives were selected according to the traditional use and the historical function, described in the Introduction. The amount of additives was selected by some preliminary tests, in order to obtain workable mixtures, maintaining the concentration of additives under the value of 5% (Cechovà et al., 2010). The following were used:

- Aged lime putty – maturation of 24 months. Manufacturer: *La Banca della Calce S.r.L.*
- Natural hydraulic lime (NHL 3.5). Manufacturer: *La Banca della Calce S.r.L.*
- Sand – dried silica sand, type "505", with grain size 0.10 ÷ 0.60 mm. Composition: SiO_2 (80.80%), Al_2O_3 (6.19%), CaO (4.60%), MgO (2.18%), Na_2O (2.00%), K_2O (1.96%), Fe_2O_3 (1,73%). Manufacturer: *Sabbie di Parma S.r.L*)
- Linseed oil – crude natural linseed oil. Manufacturer: *Maimeri S.p.A.*
- Brown sugar – common commercial product.
- Bovine milk – full fat, common commercial product, protein content about 3%, fat content about 5.5%.
- Deionized water.

The binder/aggregate ratio was selected by some preliminary tests, in order to obtain workable mixtures. This ratio (by volume) was 1:1.5 in the aged lime putty based mortars and 1:1.5:0.5 in the natural hydraulic lime based mortars. After preliminary tests, specimens of both binders were prepared in three different versions: unmodified, with 0.5% additives, and 2% additives (expressed

as % in weight). These different concentrations have been selected on the base of three important factors: maintaining the correct fluidity and workability of the mixture; obtaining a compact paste that did not drip down the trowel; avoid the liquid release of layed mortar. In order to select the right concentration of milk, the complexity of this organic material was considered. The grip acceleration effect, the hydrophobicising action and increasing effect of adhesive properties conferred to lime-based mortars by milk, are due mainly to its protein fraction. Milk is made up predominantly of water (the measured dry extract for this work was of 12.5% by weight), thus introducing it into the two different concentrations established for oil and sugar would not have a significant effect on the casein content. It was therefore decided, in the case of hydraulic lime mortars, to replace the milk to the quantity of water introduced in the base mixture (binder/aggregate/water ratio (by volume) of 1:1.5:0.5). Given the amount of ingoing milk and its dry residue, the total dry matter was 2.3% of the weight of the total. For the lime putty mortars, the suggestions proposed in the literature were followed (UNI EN 15801, 2010) for the preparation of the lime paint with milk derivatives. Thus, before being used, the casein had to mature in lime water for a few days. Given the amount of milk introduced and its dry residue, a total of dry matter represents 1.08% of weight of the total. Specimens of 5 x 5 x 2.5 cm were prepared in quadruplicate. Aged lime putty based mortar mixtures were prepared as follows:

1. sand and lime putty were mixed together with a trowel; 1a. for oil and sugar added mixtures: the additive was gradually added to lime putty before mixing all constituents with sand; 1b. for milk-added mixtures: the whole concentration of milk was added to the lime putty (the compound obtained was aged for 10 days) and then all constituents were mixed with the sand;
2. the moulds were filled in one layer.

Natural hydraulic lime-based mortar mixtures were prepared as follows:

1. for unmodified mixtures: all dry constituents (lime and sand) were mixed together with a trowel, then water was added to obtain a homogeneous mixture; 1a. For oil added mixtures: oil was added to water to create a temporary emulsion, which was then added to the lime, and then the sand was added, and all the constituents mixed together; 1b. For sugar added mixtures: sugar was solubilized in water, and this solution was added to the lime and then the sand was added, and all constituents were mixed together; 1c. for milk added mixtures: all dry constituents (lime and sand) were mixed together with a trowel, then milk was added to obtain an homogeneous mixture;
2. the moulds were filled in one layer.

The moulds were removed after two days. Specimens were used for experiments after 28 days, 3, 6 and 12 months of curing under environmental conditions (20-25°C T, 50-60% RH).

In the text the following abbreviations (Table 1) were used.

2.2. Methods

2.2.1. Colorimetric measurement

In order to identify the aesthetic modification caused by the addition of organic material in the mortars, the variations in the chromatic parameters in the CIELab colour space (1976) were determined. The three coordinates of CIELab represent the lightness of the colour (L*), its position between red and green (a*) and its position between yellow and blue (b*). A set of three series of measurements L*, a* and b* (an average of nine different small areas of specimens) at 28 days, 3, 6 and 12 months of curing on the surface of each specimen was acquired. In order to evaluate the influence of the support (such as a wall) on the uniformity of the colour of mortars made with organic substances, specimens made with the same dough as those listed in Section 2.1, but placing the mixture on a *terracotta* tile of 5 x 5 x 0.5 cm. A Minolta Chroma Meters CR 200 colour-

measuring instrument, with a 8 mm diameter spot, characterized by an integrated light source, with a fixed geometry of illumination to always ensure the same conditions of measurement, was employed. The instrument was equipped with Spectra Magic *NX Pro* software. ΔE values between the reference specimens (1, without additive) and additive specimens (2) and among the four measurement steps on the same specimen were calculated as $\Delta E^*Lab = [(L^*_2 - L^*_1)^2 + (a^*_2 - a^*_1)^2 + (b^*_2 - b^*_1)^2]^{1/2}$.

2.2.2. Physical property measurements. Determination of capillary absorption

A capillary water absorption test was performed based on (UNI EN 15801, 2010). Three copies of each type of mortar were tested at 3, 6 and 12 months of curing. Each specimen was placed on a filter paper, ground, immersed in distilled water, and placed into a sealed container to avoid evaporation. Specimens were weighed for 10 days at various time steps (10, 20, 30 minutes and 1 to 8 hours on the first day; then, once a day), measuring the increase in mass. The results were expressed in $g \cdot cm^{-2}$, as water absorption (g) for surface unit (cm^2).

2.2.3. Physical property measurements. Determination of water vapour permeability

Water vapour permeability was based on (UNI EN 15803, 2010). Three copies of each type of mortar were tested at 6 and 12 months of curing. Each specimen was placed in a vessel filled with 10 cc of distilled water; vessels with specimens were placed into a climatic chamber, with 55.0 ± 0.5% of relative humidity (RH) and 30.0 ± 0.5°C T. The relative humidity difference between the inside and outside of the cups causes moisture to flow through the porous mortar, from higher to lower RH sides. Decreases in weight were recorded once a day for 5 days. Water vapour permeability coefficients were calculated as the amount of water vapour passed through one square meter of a specimen in an hour. The results were expressed in $g \cdot m^{-2} \cdot h^{-1}$.

2.2.4. Transmitted light microscopy

Petrographic observations on thin sections of 30 μm thickness were performed to obtain the main textural-compositional parameters of the mortars at 12 months of curing. The thin sections were obtained from the center of the specimens, perpendicular to the surface. An optical transmitted light polarized microscope, Zeiss AxioScope *A.1*, with parallel and cross nicols, with 2.5X, 5X and 10X of magnification was used. The acquired images of thin sections were processed with Axiovision software.

2.2.5. UV fluorescence microscopy

Polished sections of the mortars at 12 months of curing were observed under a microscope with UV light in order to observe the fluorescence intensity of the organic materials and, accordingly, whether areas could be observed of organic material accumulation in the mortars. The polished sections were obtained from the center of the specimens, perpendicular to the surface. An Epifluorescence Microscope, Nikon Eclipse E600, with an UV-2A ultraviolet fluorescence filter was used. NIS Elements software was used to process the images acquired by a digital video camera.

2.2.6. Carbonation test using a phenolphthalein indicator

Carbonation test was based on (UNI EN 14630, 2007). Phenolphthalein is often used as an indicator in titrations: it turns colourless in acidic solutions and pink in basic solutions (over pH 8.5). This method captures the colour change boundary among uncarbonated, partially carbonated or fully carbonated concrete, at which the pH is about 9. Thus, the rate of carbonation was tested by the phenolphthalein method based on (UNI EN 14630, 2007). This test was executed on a horizontal section, parallel to the largest surface, of each specimen. An aqueous solution (100 ml) of

phenolphthalein (1 g) dissolved in 70 ml of ethanol was sprayed onto the mortars, and a photo was taken of the colour change. The test was carried out for specimens at 6 and 12 months of curing.

2.2.7. X-ray diffractometric analysis

In order to identify the influence of organic additives on the mineralogical transformation due to the carbonation and curing of different types of mortars, XRD analysis was performed. Powder samples were collected from the center of the specimens, of both raw inorganic materials (sand, natural hydraulic lime, and lime putty) and on each specimen at 28 days, 3, 6 and 12 months of curing. A PANalytical X'Pert PRO X-ray diffractometer with Cu anticathode (λ = 1.54 Å) was used, under the following conditions: current intensity of 30 mA, voltage 40 kV , explored 2Θ range between 3 ° - 70 °, step size 0.02°, time to step 50 s and scan speed of 0.04 °/s. The instrument was equipped with X'Celerator multirevelatory and High Score data acquisition and interpretation software.

2.2.8. Mechanical parameters

The mechanical tests were carried out on three specimens sized 2.5 x 2.5 x 5 cm for each type of mortar. For each specimen the maximum resistance to compression was measured, with a compression speed of 1 mm/min. A Shimadzu Autograph AG-X tester was used, connected to a computer with Trapezium-X software. The measures were taken at 6 and 12 months of curing.

3. RESULTS AND DISCUSSION

3.1. Colorimetry

Figures 2 and 3 show the differences in colour between the unmodified specimens and the specimens with additives at 28 days, 3, 6 and 12 months. All the lime putty based specimens showed high values of ΔE: for the LO2 and LM specimens the values remained constant from 28

days to one year of curing; for the LS1 and LS2 the ΔE was higher at 28 days and 3 months and decreased at 6 months and 1 year. For LO1 the greater value was reached at 6 months of curing. For the natural hydraulic lime based specimens the higher values of ΔE was observed for the LS1 and LS2 specimens at 28 days and 3months of curing. A decrease of values at 6 months was observed. For LO1 and LO2 constant values were registered. For the LM specimens the greater value of ΔE was obtained at 3 months. The different contribution of L*, a*, b* parameters in the variation of ΔE must to be considered: The colour coordinates b* and L* are characterized by the highest number of variations in the specimens prepared with linseed oil and milk. L* tended to decrease: i.e., in the lime putty specimens, the L* average values decreased from 88.69 in the reference specimens, to 80.20 in lime with 2% of oil (LO1), 85.24 in lime with 0.5% of oil (LO2), and to 75.34 in lime with milk (LM). In the hydraulic lime specimens, L* average values decreased from 73.34 in the reference specimens, to 64.44 in specimens with 2% of oil (HO2), to 69.01 in specimens with 0.5% of oil (HO1), and to 63.04 in specimens with milk (HM). The b* coordinate, on the other hand, increased: i.e., in the lime putty specimens, the b* average values increased from 1.29 in the reference specimens, to 16.09 in LO1, 6.07 in LO2, and to 6.80 in LM; in the hydraulic lime specimens, the b* average values increased from 12.49 in the reference specimens, to 14.52 in HO1, and to 13.39 in HO2.

Specimens with brown sugar showed the greatest differences with respect to the reference specimens, determined mainly by a marked decrease in brightness L*: i.e., at one year curing, the average values of L* decreased to 68.32 in HS1 and to 50.97 in LS1. However, the maximum differences were observed after 28 days of curing. The fluctuation in ΔE values over the whole curing period, especially in the sugar added specimens (both in lime putty and in hydraulic lime) were probably due to the high mobility of the organic compound in the mortars. Specimens on the

brick support, especially those with oil added, showed significantly lower values of ΔE compared with similar specimens produced in the waterproof moulds (Figure 4).

This may be due to the presence of brick, which absorbs the liquid material (oil and water) thus preventing liquid stagnation during specimen preparation. For the same reason, the colour of the mortars on the porous support was uniform over the whole surface, while some of the laboratory specimens showed obvious colour differences between the exposed side and the other surfaces (Figure 5).

3.2. Capillary water absorption

The capillary water absorption tests were performed on specimens without additives and on specimens with additives of both types of binders. For the specimens without additives, the capillarity water absorption remained unchanged from 3 to 6 months of curing, and there are no significant differences (about 0.01 $g \cdot cm^{-2}$, average values) between the lime putty and natural hydraulic lime. After one year, there was a considerable reduction in water absorbed, compared with the first measurement: 36% (lime putty) and 44% (natural hydraulic lime) (Figures 6 and 7).

Linseed oil gave a hydrophobic effect to mortars, causing a decrease in the amount of absorbed water, with respect to the reference specimens. In specimens with 2% of added oil (LO1), capillarity water absorption decreased from 3 to 6 months of curing (for example, in the lime putty specimen it decreases from 0.37 to 0.17 $g \cdot cm^{-2}$, average values), then remained almost unchanged from six months to one year. Natural hydraulic lime based specimens with 0.5% added oil (LO2) showed the same trend, whereas this trend was reversed in the lime putty-based mortar. Oil may have moved into the mortar because the lime putty was not fully carbonated at three months of curing, thus causing these oscillating results. Milk addition involved a reduction in capillarity water absorption, from 3 months to one year of curing, in both types of mortars. Also in this case, the

additive performed a hydrophobic action. Sugar is a hydrophilic material, thus it migrates inside fresh mixtures. After one year of curing, sugar did not cause significant changes in capillary water absorption, compared with the reference specimens. Linseed oil and milk, due to their hydrophobic effects, determined the lower capillary water absorption in both types of mortars. This effect was evident in the first hour of measurement and showed a stable trend over one year (Figure 8). After one year of curing, a strong decrease in capillarity coefficients was observed, above all for the specimens made of lime without additives.

3.3. Water vapour permeability

In both types of mortar, there was a general decrease in water vapour permeability, from six months to one year of curing (Figures 9 and 10). Lime putty-based specimens showed greater values of Cp compared with the natural hydraulic lime-based specimens (the largest difference between two types was observed in the mortars with milk at six months of curing); this trend is observed at both six months and one year of curing. The LM specimen (lime putty with milk) showed the highest permeability and the only significantly different value, compared with the unmodified mortar specimen. The increased permeability that milk gave to lime putty could be due to the protein fraction which has aerating properties All the organic additives added to natural hydraulic lime, increased the permeability by at least 4 $g \cdot m^{-2} \cdot h^{-1}$, compared with the reference specimens.

3.4. Optical microscopy. Observation of a thin section under transmitted light polarized microscope

The microscopic observation of a thin section of a mortar gives information on:

- binders (appearance and distribution, texture and structure);
- aggregates (composition, shape, distribution in the binder, minimum and maximum size);

- macroporosity (amount, shape, size, distribution, orientation) (Pecchioni et al., 2014; UNI EN 15803, 2010).

Lime putty-based mortars showed a higher macroporosity, with pore sizes from 300 µm to 2000 µm (average values), whereas specimens with natural hydraulic lime showed a lower amount of macropores, between 1700 µm and 300 µm (average values). The specimens with sugar presented a more compact structure compared with the milk and oil specimens. In the natural hydraulic lime specimens with additives, non fully-hydrated binder areas were clearly evident. In these mortars, with the exception of specimen HO1 (which contains 2% linseed oil), macropores were not interconnected and showed a smooth and rounded shape. The lime putty mortars had interconnected macropores with irregular shapes, and there was visible shrinkage cracks in the binder and halos between the aggregate grains and the binder. The addition of 2% brown sugar to the hydraulic lime specimens produced larger pores, but these are always round in shape. Adding milk also led to a larger size of pores than HB (unmodified specimen), but smaller than HS1 (natural hydraulic lime with 2% sugar). Thus, milk addition in the lime putty based mortars led to greater macro porosity, but the shrinkage cracks of the binder were not visible. The organic additives in hydraulic lime determined a higher porosity than the specimens with no additives, probably because they slow down the hydration of non-hydrated calcium silicates, which are responsible for the hardening of hydraulic lime.

The porosity conferred by the addition of milk, especially in the specimens with lime putty, was probably due to the air-entraining property of the proteins (Arcolao, 1998). Comparing the observation of the thin sections with the results of the capillary water absorption tests, highlighted how the hydrophobicity of the specimens due to the milk and oil do not lead to a lower porosity of the mortars (Figures 11 and 12).

3.5. Observation of polished section under optical microscope in UV fluorescence

The visible fluorescence in specimens with additives (especially with linseed oil and milk) had very different characteristics in the two types of inorganic binder, but is always higher than in the specimens without additives. In the specimens with natural hydraulic lime, the fluorescence was distributed in homogeneous yellowish spots of low intensity, whereas in the specimens with lime putty, a very strong brightness of the binder was found, which "wraps" the grains of the aggregate. UV fluorescence, on the other hand, was very weak in the specimens with natural hydraulic lime and brown sugar. The variance between the fluorescence of natural hydraulic lime and lime putty-based mortar specimens was probably due to the different consistency of the binder (the hydraulic mortar is a powder, the putty mortar is a soft paste). The different method of adding the additives during the mortar preparation (directly to the lime putty and then mixed with the aggregate) could explain the variability in the intensity of the UV fluorescence. This method of preparation leads to a better and more homogeneous distribution of the additives into the binder (Figure 13).

3.6. Carbonation test with phenolphtalein method

Natural hydraulic lime-based specimens: mortars with oil and milk were less carbonated than the unmodified mortar and the sugar-added mortars, at six months of curing. At one year of curing, only the specimen without additives is fully carbonated. However, the purple coloration was less strong in all the specimens, compared to that observed at six months. Aged lime putty-based specimens: at six months of curing, all the specimens showed a homogeneous and highly-intense purple colour, which means a very low level of carbonation. At one year of curing, the specimens without additives and with 0.5% of sugar showed the largest carbonation front (up to 2 cm from the edge). However, especially in the hydraulic lime specimens, the carbonation proceeds from the outside inwards and is still incomplete in all the specimens (Figures 14 and 15).

3.7. X-ray diffraction analyses

Quartz, plagioclases, k feldspar, micas, serpentine and other phyllosilicates make up the mineralogical composition of the sand added to the binder. For the mortars made with natural hydraulic lime, the calcium hydroxide disappeared after 28 days in the specimens without additives and in those with 2% sugar. The presence of CSH phases in the XRD patterns (the ICDD database suggests the presence of tobermorite) was only recorded in the specimens without additives at 3 and 6 months of curing ,while in the specimens with additives the presence of anhydrous calcium silicates was detected. At one year of seasoning, the specimens without additives presented abundant hydrated calcium silicate phases. The presence of additives prevents the hydration of calcium silicate phases. However, calcium silicate hydrates are often formed in the amorphous phase, and thus are not detectable by XRD (Tables 2 and 3).

For the specimens prepared with lime putty at 28 days, 3 and 6 months, the presence of Portlandite ($Ca(OH)_2$) was registered in the XRD patterns, indicating that the carbonation is still in progress. At one year, the specimens with lime putty without additives present smaller amounts of calcium hydroxide. In the specimens with additives, the calcium hydroxide was always abundant in those with 2% oil, only present in those with 0.5% oil and with sugar. In the specimens with milk added, calcium hydroxide was only detected in traces (Table 3).

3.8. Mechanical properties

The results of compressive tests on specimens without additives and with additives at one year of curing are shown in Figure 16. Regarding the reference specimens without additives, there was a difference in the compressive strength of 3.56 N/ mm^2 between the mortars made with natural

hydraulic lime and those with putty lime. The compressive strength values of hydraulic lime mortar still correspond with those reported by the supplier. In the specimens with putty lime and additives, the addition of 2% oil and milk determined a reduction in the values of compressive strength compared to the mortars without additives. There are various possible reasons for this, such as the lower degree of carbonation and/or increased porosity of mortars with oil (Cechovà et al., 2010). Oil can also partially prevent the contact between grains of aggregate and the binder. The results of putty lime-based mortars with 2% oil are comparable to values obtained in the literature. In other studies, on the other hand, the compressive strength was evaluated on specimens of cement-based mortars with added oil (Justnes et al., 2004): in this case, a comparison with the results obtained in the present study is not possible.

Sugar provided greater resistance, which increased in proportion to the concentration of the additive. Some studies (Cennini, 1971) have demonstrated how additives in the powder of aerial lime improve the compressive strength. However, these results cannot be compared because the measurements were performed at 28 days of curing and the mortars were added with 5% of organic substances. The sugar probably has an influence on the initial solidification of the mortar, producing a more compact microstructure (cfr. Section 3.4). The presence of organic additives in the specimens prepared with hydraulic lime caused a drastic decrease in the compressive strength with respect to the specimen without additives; in particular when oil was used, the resistance values of the specimens with hydraulic lime became similar to the values of the specimens with putty lime. The sugar reduced the resistance of the mortars compared to the specimens without additives in inverse proportion to the concentration of the additive, although the specimen with 0.5% sugar had a greater standard deviation. This is due to the fact that the presence of additives slows down the hydration of non-hydrated calcium silicates, which are responsible for hardening hydraulic lime.

4. CONCLUSIONS

The behaviour of mortars made with two different types of binders (natural hydraulic lime and aged putty lime) and different amounts of organic additives (linseed oil, cow's milk, brown sugar), was monitored starting from the set up to one year of curing. In two types of mortars, we highlighted a series of transformations induced by the additives, which otherwise would be impossible to observe in historic mortars. In fact not only the low concentrations of the additives, but also the secular ageing, have led to a lack of knowledge regarding the physical and mechanical properties of historic mortars made with organic additives. The final evaluation on the results obtained requires preliminary considerations. The results obtained in this research can be only partly compared with other data from past studies, because they involved different preparation methods, types of ingredients and seasoning times. In fact, there is no single protocol for this kind of research. Is therefore crucial to standardize not only the analytical methodologies, but also the techniques of creation and the materials of laboratory specimens. Secondly, some specimens (i.e. putty lime based mortars) were at a premature step of carbonation (unfinished or not having stabilized). This affected the validity of some of the tests, however it provided the opportunity to observe the behaviour of the mortars during curing, in relation to the presence/absence of organic additives. The changes observed in various specimens, which however in some cases were non-linear, are in agreement with the hypothesis that historic mortars were not manufactured simply by following fixed recipes but on the basis of empirical knowledge of the raw materials. With respect to the aesthetical parameters, a general modification of the colour for the mortars was found over time.

Generally, colour differences tended to decrease over the six months, stabilizing after one year of seasoning. The different values of ΔE registered, due prevalently to L* and b* parameters, are linked to the distribution of additives in the mixture and to the tendency to stabilize over time. The colour variations of the specimens on the *terracotta* tile support, compared to those created in the waterproof frames, are lower because the support helps to absorb most of the excess liquid. These results show the suitability of the additives such as linseed oil for wall paintings and coating plasters. With respect to the physical properties, oil and milk led to, for both types of inorganic binder, the lower values of capillary water absorption. This hydrophobic effect appears to be relatively stable over time. The water repellence conferred is not, however, accompanied by the closing of pores, as shown by the permeability and porosity tests and the observations of thin sections that revealed that porosity was maintained. In the mortars based on hydraulic lime, the presence of additives increased the permeability coefficient, whereas for the mortars based on putty lime, the milk led to a significant increase in permeability, thus confirming the aerating action exerted by the protein fraction present in this additive (Arcolao and Dal Bo', 2001; Jasiczak and Zielinski, 2006; Chandra and Aavik, 1987). Observations on the porosity were also confirmed by the analysis of thin sections, which also revealed the different morphology of the pores in the two types of lime. In the putty lime-based mortars, with or without additives, larger pores than those in the natural hydraulic based mortars were observed, due to the different morphology of the two binders (Cechova at al., 2010). With observation under UV fluorescence, the polished sections showed a different distribution of the additives in the two types of inorganic binders. In addition the state of aggregation of the binders (solid powder or soft paste) and the procedures for the addition of additives in the mixture led (in terms of distribution) to very different results (point-shaped oil distribution on aerial lime based mortars, when the oil is added to the sand and the binder powder) (Cechova at al., 2010). The presence of additives in mortars made with natural hydraulic

lime hindered the hydration of calcium silicates (Cechova at al., 2010), leading to a decrease in compressive strength, as also confirmed by XRD analysis and by the higher porosity conferred to the mortars. Also in the mortars with putty lime and additives, the addition of oil and milk determines a decrease in compressive strength compared to the specimens without additives. The sugar confers, in contrast, a greater strength to the lime putty mortars, which increases proportionally to the concentration of the additives (sugar would seem to favor the cohesion of the aerial lime based mortars thanks to the calcium saccharate formation) (Rattazzi, 2007). The chemical structure of a disaccharide probably interacts with calcium hydroxide in hardening process, facilitates the formation of calcite with more compact structure (Yang et al., 2010). In the hydraulic lime mortars, instead, the retarding action of sugar is probably due by the prevention of the formation of calcium silicate hydrate (CSH) (Khan and Baradan, 2008). Monitoring the specimens for up to 12 months of curing highlighted a series of transformations induced by the additives, which otherwise would be impossible to observe. The results thus demonstrate the importance of a thorough study of the correlation between the properties and composition of mortars.

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Figures captions:

Figure 1. Specimens in the moulds.

Figure 2. Lime putty based specimens; ΔE between specimens without additives and specimens with additives. Values measured at 28 days, 3 months, 6 months and 1 year of curing.

Figure 3. Natural hydraulic lime-based specimens; ΔE between specimens without additives and specimens with additives. Values measured at 28 days, 3 months, 6 months and 1 year of curing.

Figure 4. Lime putty based specimens on support; ΔE between specimens without additives and specimens with additives. Values measured at 28 days, 3 months, 6 months and 1 year of curing.

Figure 5. Colour homogeneity difference between a specimen prepared in a waterproof mould (on the left) and the same mortars on a porous support (on the right).

Figure 6. Lime putty-based specimens; Qi values at 3, 6 months and 1 year of curing.

Figure 7. Natural hydraulic lime based specimens; Qi values at 3, 6 months and 1 year of curing.

Figure 8. Q_i trends (average values) during the first hour of measurement. L = lime putty and sand without - additives, H = natural hydraulic lime and sand without additives, O = with linseed oil, S = with brown sugar, M = with bovine milk, 1 = 2% of additive, 2 = 0.5% of additive.

Figure 9. Lime putty-based specimens; C_p values at 6 months and one year of curing.

Figure 10. Natural hydraulic lime-based specimens; C_p values at 6 months and one year of curing.

Figure 11. Thin sections of specimens, zoom 2.5x, XN. Different kinds of macropores. On the left (HO1 thin section, lime putty with 2% of oil), macropores are partly interconnected and have an irregular shape; on the right (HS1 thin section, hydraulic lime with 2% of sugar), macropores are not interconnected and have a rounded shape.

Figure 12. Thin section of specimen LO1 (lime putty with 2% of oil),, zoom 5x, XN. A focus on high-interconnected ad irregular shaped macropores.

Figure 13. Polished sections under optical microscope in UV fluorescence, zoom 10X. On the left, the HO1 specimen (natural hydraulic lime with 2% linseed oil) shows a lower fluorescence intensity compared, on the right, with LO1 specimen (aged lime putty with 2% linseed oil). At the bottom, the LB specimen shows a lower UV fluorescence compared with LO1.

Figure 14. Carbonation test. From left to right: LO1 (lime putty with 2% of oil), HB (hydraulic lime without additives), HO1 (hydraulic lime with 2% of oil) at one year of ageing. Purple indicates low carbonation.

Figure 15. Carbonation test. From left to right: LO1 (lime putty with 2% of oil), HB (hydraulic lime without additives), HO1 (hydraulic lime with 2% of oil) at six months of ageing. Purple indicates low carbonation.

Figure 16. Compressive tests performed at 1 year of curing on specimens without additives and with organic additives.

Tables captions:

Table 1. List of abbreviation used for the specimens.

Table 2. Mineralogical composition of the specimens made with natural hydraulic lime at one year of curing.

Table 3. Mineralogical composition of the specimens made with aged lime putty at 1 year.