Construction and Building Materials 31 (2012) 135-143

Contents lists available at SciVerse ScienceDirect

Construction and Building Materials

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

Aerial lime-based mortars blended with a pozzolanic additive and different admixtures: A mineralogical, textural and physical-mechanical study

A. Arizzi*, G. Cultrone

Universidad de Granada, Departamento de Mineralogía y Petrología, Campus Fuentenueva s/n, 18002 Granada, Spain

ARTICLE INFO

Article history: Received 13 June 2011 Received in revised form 12 December 2011 Accepted 23 December 2011

Keywords: Metakaolin Perlite Water-retaining agent Plasticiser Pore system Mechanical strength

ABSTRACT

This work deals with the effects of a lightweight aggregate, plus water-retaining and a water-reducing agents on the hardened properties of mortars in which the aerial lime is replaced by a 10% and 20% metakaolin content. The influence of different binder-to-sand ratios (1:3, 1:4, 1:6, 1:9 by weight) is also investigated here. A tight relationship between metakaolin content and mortar physical-mechanical properties (compressive strength and pore system) has been found. This study is especially helpful for the establishment of the adequate proportions of additives and admixtures to be used in aerial lime mortars designed for restoration works.

© 2011 Elsevier Ltd. All rights reserved.

1. Introduction

The addition of inorganic or organic substances to artificial materials such as mortars and bricks is an ancient practice in the field of construction. There are evidences that many organic materials, especially proteins-based (i.e. blood, hair, straw, milk, eggs) [1] were used in the elaboration of historic mortars, in order to improve their workability, resistance and hardening.

Nowadays, although practices and materials have changed and new performances are required in modern constructions, additions are essential components of masonry materials, especially concrete. These additions are divided in two groups: *additives* (i.e. pozzolans, mineral fillers, ceramic powder) that are used in lime based mortars with the aim to improve certain properties or obtain special performances mainly related to the increase of mortar strength, and *admixtures*, added in low amounts (i.e. not higher than a 5% of the total mass) in order to produce a permanent modification in the fresh or hardened mortar, such as density decrease, workability improvement or waterproofing.

The use of lime as binder in mortars involves well-known inconveniences (i.e. slow setting and carbonation times, high drying shrinkage, low mechanical strength) [2] that, in the last 50 years, have been overcome with the use of Portland cement. On the other hand, the ill-omened effects of the use of Portland

cement in the Architectural Heritage [3,4] have forced workmen, restorers and scientists to find out alternative materials apt to improve the performances of lime-based mortars. In this sense, it is opportune to use specific admixtures, such as air-entraining and water-retaining agents and pozzolans, which improve workability in the fresh state, and mechanical strength, water permeability and frost resistance in the hardened state of lime-based mortars.

The effects that some admixtures (i.e. water-retaining agents, air-entraining agents and water repellents) have on fresh and hardened performances of air lime-based mortars were almost unknown until the last decades, because the research on these substances was limited to concrete and cement mortars [5]. Only recently, researchers have demonstrated interest in highlighting the advantages and disadvantages of the use of admixtures on aerial lime pastes [6] and aerial lime mortars [7-10]. Nevertheless, none of these studies deals with the effect that those admixtures have on mortars in which a pozzolan is blended to the binder (aerial lime). There exist many evidences of the use of pozzolanic materials, such as brick pebbles or dust and calcined clays [11,12], in ancient mortars. Pozzolans were used in combination with lime to improve the resistance to moisture of rendering mortars, the compactness of floor bedding mortars and the mechanical strength of structural mortars [13,14]. Nowadays, the addition of pozzolanic additives (i.e. fly ashes, silica fumes and calcined clays) to aerial lime mortars is recommended because they confer good properties in the early age, high values of mechanical strength, low water permeability, good cohesion between binders and aggregates and durability [15-20].





^{*} Corresponding author. Tel.: +34 58246614; fax: +34 958243368. *E-mail address:* arizzina@ugr.es (A. Arizzi).

^{0950-0618/\$ -} see front matter © 2011 Elsevier Ltd. All rights reserved. doi:10.1016/j.conbuildmat.2011.12.069

Our aim is to study the changes in mineralogical, textural and physical-mechanical characteristics caused by the addition of different admixtures (both organic and inorganic) in mortars composed by a calcareous aggregate and an aerial lime blended with metakaolin. Three types of admixtures have been considered and blended together or individually in mortars: a lightweight aggregate (perlite), a water-retaining agent (cellulose derivative) and a plasticiser (polycarboxylate). The study of the fresh properties of mortars is not considered here, since the effectiveness of these admixtures in exerting their function is already known within the scientific community [5,8,10,21,22]. On the other hand, there is a lack in the petrophysical characterisation of partially carbonated mortars with such mixtures. For this reason, the characteristics of mortars will be investigated after 60 days since their elaboration.

Perlite is an obsidian derivative that is transformed into a very light, porous and fire resistant material, after a rapid heating at temperatures between 900 and 1100 °C. It has a low density, due to the formation of bubbles inside it that cause an expansion up to 15–20 times its original volume. Perlite is used as additive in mortars, concrete and bricks because it provides thermal insulation, reduces fissures and improves long-term mechanical performances [21] and durability [22].

The cellulose derivative increases the adhesion power of mortar and controls the water retention capacity in the fresh state [23], thus lowering the shrinkage during drying and the water film formation. It confers an initial high consistence to the mortar, although this is not maintained during the mortar application phase (consistence changes from very high to moderate).

On the other hand, the polycarboxylate is a synthetic polymer that, by dispersing the lime particles, supplies a high maintenance of the mortar workability and reduces the voids content [24].

This study deals with the morphological, textural, mineralogical and physical-mechanical modifications that the addition of these admixtures produces in mortars, when added alone or blended together. One part of the study refers to mortars in which these admixtures are blended in different combinations whilst the binder-to-aggregate ratio is maintained fix. Another part focuses otherwise on the modifications that occur in mortars prepared with fixed amount of the same admixtures but different binderto-aggregate ratios.

2. Materials and methods

All mortars were prepared with a calcitic dry hydrated lime (CL90-S, [25]) produced by ANCASA (Seville, Spain) and a calcareous aggregate (CA) with a continuous grading from 0.063 to 1.5 mm. The pozzolan used is a metakaolin (MK) (CLASS N POZZOLAN, [26]), produced by Burgess Pigment Company (USA).

The chemical composition (major and minor elements) of these components (CL, CA and MK) was studied by means of a Bruker S4 Pioneer X-ray fluorescence spectrometer (XRF) (with wavelength dispersion equipped with a goniometer that analyses crystals (LIF200/PET/OVO-55) and Rh X-ray tube (60 kV, 150 mA)), as it is shown in Table 1. The mineralogy of metakaolin was also characterised by means of X-ray diffraction, using a Philips PW-1710 (disoriented powder method, analysis conditions: radiation Cu K α (λ = 1.5405 Å), 3–60° 2 θ explored area, 40 kV voltage, 40 mA current intensity and goniometer speed of 0.1° 2 θ /s), and its X-ray pattern is shown in Fig. 1.

Table 1

Chemical composition of the calcitic lime (CL), calcareous aggregate (CA) and metakaolin (MK).

Oxides (%)	CL	CA	МК
SiO ₂	0.35	0.16	50.84
CaO	78.01	59.59	0.22
SO ₃	1.39	0.03	0.09
MgO	0.70	0.87	0.66
Fe ₂ O ₃	0.10	0.04	0.44
Al_2O_3	0.18	0.06	45.26
K ₂ O	0.05	0.01	0.24
P_2O_5	0.04	0.01	0.17

Eight mixtures were prepared with different binder/sand (B/S) ratios, metakaolin-to-binder proportions and admixtures amounts, as shown in Table 2.

The flow of the fresh mortar pastes, determined according to the European Standard EN 1015-3 [27], is comprised between 120 and 150 mm. Mortars were conserved during 7 days in normalised steel moulds $(4 \times 4 \times 16 \text{ cm})$ at $T = 20 \pm 5 \,^{\circ}$ C and RH = $60 \pm 5\%$, instead of being cured at a RH of 95\%, following the modification of the standard EN 1015-11 [28] proposed by Cazalla [2]. Despite the presence of metakaolin, the mortars studied here are not hydraulic mortars but aerial ones, hence the preference of curing them at conditions that favour carbonation more than hydration.

After desmoulded, they were cured at the same conditions of T and RH for 60 days in total. Then, mineralogical, morphological and textural characteristics of mortars were determined.

The mineralogical phases of both internal and external zones of mortar samples were determined by means of two different techniques: thermogravimetry (TGA) and X-ray diffraction (XRD). In the first case, it was employed a Shimadzu TGA-50H thermogravimetric analyser, working in air in a temperature range of 25–950 °C, with a heating speed of 5 °C/min. For the XRD analysis, it was used a Panalytical X'Pert PRO MPD diffractometer, with automatic loader and X'Celerator detector, 4–70° 2 θ explored area. The identification of the mineral phases was performed by using the X-Powder software package [29].

For the textural study, mortars fragments were metalized with a carbon layer and the microstructure analysed by using a Carl Zeiss Leo-Gemini 1530 field emission scanning electron microscope (FESEM).

Open porosity (P_o , %) and pore size distribution (PSD, in a range of 0.002 < r < 200 µm) were determined using a Micrometics Autopore III 9410 porosimeter (mercury injection porosimetry, MIP). Mortar fragments of ca. 1 cm³ were oven-dried for 24 h at 60 °C before the analysis.

Flexural and compressive strength were measured by means of a hydraulic press INCOTECNIC-Matest. According to the EN 1015-11 [28] standard, flexural assays were carried out on three samples per mortar (of $4 \times 4 \times 16$ cm). The six samples obtained after the flexural rupture were used for the compressive assays.

3. Results and discussion

3.1. Mineralogical phases of mortars

The XRD patterns of the core (IN) and the surface (EX) of mortars are shown in Fig. 2. The main phase formed in mortars is calcite (CC, Fig. 2) because of the high presence of calcium carbonate as aggregate and also because of the carbonation of lime. The portlandite amount found in mortars after only 28 days of carbonation is low compared to the quantity that is likely to be found in aerial lime-based mortars without admixtures. This is because a part of the portlandite dissolved in water transforms into calcite (i.e. carbonation) whilst another part is involved in the lime-pozzolan reactions (i.e. hydration) favoured by the alcaline environment. The fact that mortars prepared with a lower amount of metakaolin (CCMPCR3-9 with 10% of MK on the total binder) show slightly higher peaks of unreacted lime (i.e. portlandite) in their X-ray diffraction patterns (Fig. 2) confirms that a faster lime consumption does not indicate a quicker carbonation but only the development of hydrated phases.

Calcium alluminate and silicate hydrates of variable steichiometry are formed after activation of the alluminate and silicate phases of metakaolin, in presence of calcium hydroxide (i.e. portlandite) and water [30]. By means of XRD analysis, three general hydrated phases were detected: CSH, (CaO-SiO₂-H₂O) or calcium silicate hydrates; CASH, (CaO-Al₂O₃-SiO₂-H₂O) or calcium alumina silicate hydrate; and CAĈH, (Ca₄Al₂(CO₃)(OH)₁₂·6H₂O) or monocarboalluminate. The latter is one of the mono-phase calcium hydrates and derives from the reaction between the reactive alluminates of metakaolin and the CO_3^{2-} ions present in mortars [31]. In mortars with fixed amount of admixtures, lower metakaolin content and different B/S ratios (i.e. CCMPCR3-9), CAĈH phases have precipitated in very low amounts compared to the other mortars, and they have been detected only in the internal part of the mortars (Fig. 2). Calcium silicate hydrates (CSH) and calcium alumina silicate hydrate (CASH), which are among the main hydrated phases formed at room temperature after pozzolanic reaction of metakaolin [30,32,33], were detected in very low amounts by



Fig. 1. X-ray diffraction pattern of the metakaolin. Qtz = quartz.

Table 2

Proportions of components used in the elaboration of the eight mortar types. Abbreviations indicate: binder-to sand ratio (B/S, by weight); metakaolin (MK, in% of the total weight of the binder); perlite (P); cellulose derivative (C); polycarboxylate (R). The symbols – and X indicate the absence and presence of the corresponding phase, respectively. The total amount of admixtures does not exceed the 2% of the total mass. The amount of kneading water (as % of the total mass) was determined in order to obtain a paste with a flow comprised between 120 and 150 mm (UNE-EN 1015-3 [21]).

Mortars name	Components name and proportions					Water
	B/S	MK	Р	С	R	
ССМ	1:3	20	-	-	-	31.5
CCMP	1:3	20	Х	-	-	30.5
CCMPC	1:3	20	Х	Х	-	27.5
CCMPCR	1:3	20	Х	Х	Х	29.0
CCMPCR3	1:3	10	Х	Х	Х	28.0
CCMPCR4	1:4	10	Х	Х	Х	26.5
CCMPCR6	1:6	10	Х	Х	Х	21.5
CCMPCR9	1:9	10	Х	Х	Х	20.0

means of X-ray diffraction because of their low crystallinity and reflecting powder.

CSH and different calcium alluminate hydrates (CAHs) were also detected by means of thermogravimetric analysis (TGA). The thermal decomposition of CSH occurs at temperature comprised between 100 and 125 °C, whilst CAH decompose in a temperature range equal to 150–310 °C. According to Saikia et al. [34], in the latter range of temperature both CAH and CASH decompose. Also portlandite and calcite were determined in the ranges of temperature of 350–480 and 650–900 °C, respectively.

As it was expected, carbonation is more extended in the surface than in the core of mortar as indicated by the higher peaks of portlandite obtained in the internal samples.

3.2. Textural characteristics of mortars

The textural aspect of mortars (porosity, compactness, cohesion between aggregate grains and matrix, amount of the different phases) is shown in Fig. 3. In general, the core of mortars appears more porous than the surface, and this is due to the fact that carbonation proceeds from the exterior to the interior of mortar (see differences between EX and IN, in the FESEM images of Fig. 3).

Mortars with fixed B/S ratio show a similar cohesion and porosity (Fig. 3a–d), whilst some differences of compactness were found in mortars with different B/S ratios (Fig. 3e–h). In CCMPCR mortars with bigger lime content (1:3 and 1:4 B/S ratios, Fig. 3e and f) the aggregate grains are not easily distinguished at low magnification because they appear completely recovered by the matrix. Whereas, in mortars with bigger amount of sand (1:6 and 1:9 B/S ratios, Fig. 3g and h), this cohesion is worse and isolated grains of



Fig. 2. X-ray diffraction pattern of external (EX) and internal (IN) zones of mortars with different amounts of admixtures and fixed B/S ratio and mortars with different B/S ratios and fixed amount of admixtures. CC = calcite, CH = portlandite, CAĈH: monocarboalluminate; CSH: calcium silicate hydrate; CASH: calcium alumina silicate hydrate; Qtz: quartz.



Fig. 3. FESEM images of the eight types of mortars: differences in mortars texture between the surface (EX) and the core (IN) of CCM (a), CCMPC (b), CCMPCR (d), CCMPCR3 (e), CCMPCR4 (f), CCMPCR6 (g) and CCMPCR9 (h).

aggregate can be observed. This indicates that the latter mortars are characterised by a lower compactness.

3.3. Morphology of the hydrated phases

Aluminates (as CAĈH) crystallise as hexagonal platelets similar to those of portlandite but normally larger and thinner [30] (Fig. 4a–f). Generally, they appear tangled in the mortar matrix, in some cases randomly oriented (Fig. 4a and b) and in others in form of overlapping sheets oriented perpendicularly to the basal plane, along the [001] direction (Fig. 4c–e). Bigger quantity of aluminates was found in CCM at higher magnifications (Fig. 4a and c). On the other hand, few aluminate phases were found in mortars with different B/S ratios (i.e. CCMPCR3-9). As shown in Fig. 4f, they have smaller size (almost 2 μ m) and they occasionally share one plane.

The common morphologies that calcium silicate hydrate $(CaO-SiO_2-H_2O, i.e. CSH)$ phases adopt after precipitation are: fibres (Fig. 4g), flakes (Fig. 4h), honeycomb structure (Fig. 4i), and reticular network (Fig. 4j). In CCMPCR3 and CCMPCR4 mortars all the calcium silicate morphologies were observed (Fig. 4i and j) whilst in the other mortars only fibres (Fig. 4g) and flakes (Fig. 4h) of CSH were recognised. CSH phases do not appear in CCM at the magnification of $5000 \times$ (Fig. 3a EX and IN), whilst they are visible in CCMP (Fig. 3b) and in lower quantity in CCMPC (Fig. 3c) and CCMPCR (Fig. 3d), always in the internal zone (IN) of the samples. This is an unexpected finding, given that these mortars were prepared with the highest quantity of metakaolin (Table 2). On the other hand, a much bigger amount of CSH was observed in CCMPCR3-9 mortars at the same magnification (Fig. 3e–h) and few evidences of aluminates were found. The amount of CSH phases

seems to decrease with decreasing the lime content of mortars, being the biggest in CCMPCR3 (Fig. 3e) and CCMPCR4 (Fig. 3f), and the lowest in CCMPCR6 (Fig. 3g) and CCMPCR9 (Fig. 3h).

3.4. Morphology of the organic and inorganic admixtures

Perlite has a peculiar empty structure formed by big and ordered circular cavities (around $10-20 \,\mu$ m in size) (Fig. 5a–c) that confers lightness to the mortar. Notwithstanding, it appears as a very fragile structure that is broken in many big fragments dispersed in the matrix (Fig. 5d). In CCMPCR mortars the porous structure of perlite was not observed in any sample, and only its fragments were found in the matrix. It is likely that the processes of mixing and kneading of the mortar, as well as the mechanical tensions produced during carbonation and hydration processes, cause the rupture of the perlite structure.

No evidences of the presence of the other admixtures (C and R, see Table 2) were found by means of FESEM observations.

3.5. Characteristics of the pore system of mortars

3.5.1. Open porosity value

The values of open porosity of the surface and the core of mortars are presented in Table 3. Mortars that present the highest porosity values (CCM, CCMP, CCMPCR) were prepared with the highest amount of kneading water (from 29% to 31.5%, see Table 2). The porosity is lowered by about 3% in CCMPC mortar, because of the effect of the cellulose derivative (C) that retains the water longer in the matrix, like this preventing a rapid evaporation and the porosity formation. The introduction of the polycarboxylate



Fig. 4. FESEM images of the hydrated phases (aluminate and silicate) formed after pozzolanic reaction in mortars: hexagonal AFm platelets randomly oriented observed in CCM (a) and CCMPCR (b); overlapping sheets of aluminate observed in CCM (c) and CCMPC (d); aluminate crystals oriented along the [001] direction in CCMPC (e); smaller AFm crystals precipitated in the matrix with hexagonal habit and identical orientation in CCMPCR3-9 mortars (f); CSH fibres in CCMP (g) and CSH isolated flakes in CCMPCR (h); honeycomb structure (i) and reticular network (j) of silicate hydrates in CCMPCR3-9 mortars.

causes the porosity to be higher in the interior than in the surface of mortars (see all CCMPCR and CCMPCR3-9 mortars compared to the others, Table 3) that, in this case, indicates a normal behaviour of lime mortars, in which carbonation reduces porosity at the surface more than in the interior. This fact may indicate that the lime particles dispersion induced by the polycarboxylate gives place to an improvement of the lime reactivity towards CO_2 . This difference of porosity between the surface and the core is constant in CCMPCR3-9 mortars, where the external samples showed a reduction of porosity by about 2% with respect to the internal ones.



Fig. 5. FESEM images of perlite in mortars: porous structure of this admixture observed in CCMP (a and b (detail)) and CCMPCR (c); fragments of perlite within the matrix of CCMPCR3-9 mortars (d).

Table 3

Results of the mercury intrusion porosimetry (MIP) analysis and the mechanical assays on the eight types of mortar: open porosity (P_o , in%) of the external (Ex) and internal (In) zones of samples, flexural (R_f , in MPa) and compressive (R_c , in MPa) strengths.

Mortar name	MIP analysis		Mechanical assays	
	Zone	Po	R_f	R_c
ССМ	Ex In	43.3 ± 0.6 34.2 ± 6.6	0.38 ± 0.3	7.18 ± 1.1
ССМР	Ex In	42.7 ± 0.4 40.7 ± 0.6	2.72 ± 0.3	8.57 ± 0.7
CCMPC	Ex In	39.1 ± 0.1 33.5 ± 2.5	3.04 ± 0.2	8.27 ± 0.2
CCMPCR	Ex In	41.1 ± 0.8 44.1 ± 1.3	3.44 ± 0.1	11.96 ± 0.4
CCMPCR3	Ex In	37.8 ± 4.1 39.9 ± 6.2	1.41 ± 0.2	3.35 ± 0.1
CCMPCR4	Ex In	33.1 ± 0.1 35.9 ± 0.3	1.69 ± 0.2	3.48 ± 0.1
CCMPCR6	Ex In	30.9 ± 0.1 32.7 ± 0.2	1.86 ± 0.1	3.63 ± 0.3
CCMPCR9	Ex In	30.4 ± 1.3 32.2 ± 0.5	0.07 ± 0.1	3.05 ± 0.2

CCMPCR and CCMPCR3 mortars, which differ only for the metakaolin and water dosage, show a porosity difference of about 4%. This suggests that in lime-based mortars an amount of metakaolin above 10% of the total binder gives place to a porosity increase. This is not in agreement with Frías and Cabrera'statement [35], who found that MK contents have no effect on the total porosity of metakaolin–cement pastes. On the other hand, the decrease of porosity found from mortar 1:3 to 1:9 must be related only with the different amounts of water used according to the initial lime content, since the MK proportion on the total binder is the same in these mortars.

3.5.2. Pores size distribution curves (PSDs)

The main peak obtained in all samples corresponds to pores whose radius is comprised between 0.1 and 1 µm and whose volume is the most influent on the total porosity of mortars (Fig. 6). This is a structural peak, typical of lime pastes, whose height and width normally depend on the amount of kneading water [36]. Here, the presence of metakaolin makes the dependence between water content and pore size distribution not as clear as in lime mortars, since a part of the water is consumed during the pozzolanic reaction. In CCMPC and CCMPCR the main peak is wider because a new small peak appears, contiguous to the main one and corresponding to bigger radius (around 0.6 µm). This peak has been observed also in MK-OPC pastes with MK contents up to 10% after 28 days of curing [35] and it is produced by the presence of metakaolin. Here, the peak at 0.6 µm is only evident in CCMPC and CCMPCR, perhaps because in the other mortars it is hidden by the peak at 0.1 and 1 μ m.

In all mortars a second minor peak of pores whose radius is comprised between 0.01 and 0.1 µm is present. The presence of metakaolin results in the development of these smaller pores [35] normally formed by the network of hydrated calcium silicates (the range of these pores is $0.01 < r < 0.04 \mu m$, according to Pandey and Sharma [37]). The volume of these pores is much higher in mortars with 20% of metakaolin. Among these mortars, this peak is slightly bigger in CCMP, CCMPC and CCMPCR, in which more CSH phases were observed. In general, it appears slightly shifted to smaller radius in the internal samples. Mortars with only a 10% of metakaolin present a significant reduction of the volume of these pores. This suggests that the degree of hydration in CCMPCR3-9 mortars is lower with respect to the others, even if a bigger quantity of CSH phases has been observed during FESEM observations. Moreover, by comparing CCMPCR3-9 mortars PSD curves (Fig. 6), one can notice that the volume of these pores is slightly bigger in CCMPCR3 and CCMPCR4, which were prepared with a higher content of binder (i.e. lime + metakaolin).

These findings confirm that pores with radius in the range of $0.01-0.1 \ \mu m$ are formed because of the presence of metakaolin and they indicate that these pores constitute a significant part of the pore system only when metakaolin is added to the binder in proportions bigger than 10%. Another important deduction that must be made according to the PSD curves obtained for CCMPCR3-9 mortars is that their pore system is similar to that of mortars with only calcitic lime and calcareous aggregate (i.e. without the addition of pozzolans and admixtures) which are almost exclusively characterised by pores in the range of $0.1-1 \ \mu m$ in size [38]. In addition to have the same pore system, CCMPCR mortars are characterised by a much lower porosity, which is a positive aspect in relation with their durability.

The presence of perlite does not affect the pore size distribution, which is similar to that obtained for CCM samples (Fig. 6). The pores of the unbroken structure of perlite observed in some zones by means of FESEM (Fig. 5a–c), whose main size is $20 \,\mu$ m, do not appear in these curves probably because the pressure of mercury during the MIP analysis destroys this structure, which seems to be very fragile, as discussed in Section 3.4.

3.6. Mechanical properties of mortars

As shown in Table 3, mechanical strengths (both R_f and R_c values) of mortars with a pozzolan and other admixtures are much higher than those of aerial lime-based mortars composed by only lime and aggregate (up to 2 MPa) [39,40].

We have obtained increasing values of compressive and flexural strengths with increasing aggregate proportions, except for the mortar with the lowest B/S ratio (CCMPCR9). The function of the aggregate in a mortar stays in conferring volume stability to the lime paste and in improving its mechanical resistance. Notwith-standing, a too high content of aggregate may result in a mortar with poor cohesion between the grains (low binding ability) and, consequently, with lower mechanical resistances.



Fig. 6. Pore size distribution curves of external (Ex) and internal (In) zones of mortars. The radius of pores (r, in µm) is represented in function of the incremental volume of mercury intruded (DV/Dlogr, in cm³/g).

The values of mechanical strengths of mortars also indicate that a 20% of metakaolin content produces a larger enhancement of the mechanical strengths, compared to a 10% metakaolin content, which has produced values of compressive strength between twice and three times lower. This finding is in agreement with a previous study carried out by Wild et al. [41] on metakaolin–cement pastes, in which the optimum amount of metakaolin in replacement of OPC for the strength enhancement was found to be about 20%.

The presence of admixtures affects strongly the compressive resistance of the mortars prepared with 20% of metakaolin. An increase of R_f and R_c is obtained with the addition of perlite and, mainly, of the polycarboxylate because of its ability in dispersing the lime particles and thus reducing the quantity of voids in the matrix [24]. On the other hand, the cellulose derivative decreases slightly the mortar compressive strength, as also found by other authors [5,7].

4. Conclusions

This study aimed to find out differences in the mineralogical, morphological and textural characteristics and in the mechanical properties of aerial-lime based mortars induced by the addition of a pozzolanic additive (metakaolin) and inorganic (perlite) and organic (cellulose derivative and polycarboxylate) admixtures.

It has been observed that the pozzolan leads to the formation of hydrated phases such as CSH, CASH and CAĈH, whilst the perlite, the cellulose derivative and the plasticiser do not produce any mineralogical and morphological change in mortars. The amount of the hydrated phases was found to be small according to the Xray diffraction analysis, whilst many non-crystalline CSH phases have been observed by means of scanning electron microscopy, especially in samples with 10% of metakaolin.

Important variations of the open porosity values have been found in all mortars, as consequence of the amount of water used for their preparation, which in turn is affected by the presence of the organic admixtures. On the other hand, the only additional component that affects the pore size distribution is the pozzolan, which leads to the formation of pores with radius comprised between 0.01 and 0.1 μ m. It is fundamental to point out that this family of pores is only present in mortars prepared with 20% of metakaolin content on the total binder, whilst the pore system of mortars with 10% of metakaolin is closer to that of aerial lime mortars without additives.

The addition of 20% of metakaolin also causes a bigger strength enhancement. Among the mortars prepared with the lowest metakaolin content (10%), those with higher content of binder (i.e. lime + metakaolin) are characterised by higher porosity values and lower mechanical strength. Notwithstanding, it has been found that the use of a binder-to sand proportion higher than 1:6 does not lead to any change in the pore system (open porosity value and pore size distribution) but instead produces a decrease in the mechanical strength of mortar.

This paper demonstrates that, by establishing adequate proportions of pozzolanic additives and admixtures, it is possible to improve mortars properties without modifying excessively the original characteristics of the aerial lime mortar. This aspect is crucial in the design of aerial lime-based mortars that have to be applied in restoration works. In this sense, we have demonstrated that it is possible to overcome the inconveniences of the application of an aerial lime based mortar (for example, slow hardening process and high porosity) by means of the use of additives in adequate proportions, at the same time avoiding undesired modifications of the hardened properties (for example, an excessive improvement of the mechanical strength), which might cause incompatibility with the original materials. In view of these results, we consider that a metakaolin content of 10% on the total binder, a B/S proportions between 1:4 and 1:6 and a total amount of admixtures lower than 2% on the total mass can be the appropriate dosages for the obtaining of compatible and durable repair mortars with good workability in the fresh state, low shrinkage and low mechanical strengths, which can be used, for example, as rendering materials.

Acknowledgements

This study was financially supported by Research Group RNM179 of the Junta de Andalucía and by Research Project P09-RNM-4905. We are grateful to ARGOS DERIVADOS DEL CEMENTO, S.L. for providing the raw materials used in this study.

References

- RILEM TC 203-RHM: Repair mortars for historic masonry. Testing of hardened mortars, a process of questioning and interpreting. Mater Struct 2009; 42:853– 65.
- [2] Cazalla O. Morteros de cal. Aplicación en el patrimonio histórico. PhD thesis. Universidad de Granada; 2002.
- [3] Veniale F, Setti M, Rodriguez-Navarro C, Lodola S, Palestra W, Busetto A. Thaumasite as decay product of cement mortar in brick masonry of a church near Venice. Cem Concr Compos 2003;25:1123–9.
- [4] Callebaut K, Elsen J, Van Balen K, Viaene W. Nineteenth century hydraulic restauration mortars in the Saint Michael's Church (Leuven, Belgium). Natural hydraulic lime or cement? Cem Concr Res 2001;31:397–403.
- [5] Edmeades RM. Hewlett PC cement admixtures. Lea's chemistry of cement and concrete. 5th ed. Arnold; 1998.
- [6] Ruiz-Agudo E, Rodriguez-Navarro C. Effects of additives on lime putty rheology: applications in the design of mortars for conservation purposes. In: Proceedings 1st historical mortars conference, Lisbon; 2008. p. 24–6.
- [7] Paiva H, Esteves LP, Cachim PB, Ferreira VM. Rheology and hardened properties of single-coat render mortars with different types of water retaining agents. Constr Build Mater 2009;23:1141–6.
- [8] Seabra MP, Paiva H, Labrincha JA, Ferreira VM. Admixtures effect on fresh state properties of aerial lime based mortars. Constr Build Mater 2009;23:1147–53.
- [9] Izaguirre A, Lanas J, Alvarez JI. The use of water-repellent admixtures on the behaviour of aerial lime-based mortars. Cem Concr Res 2009;39:1095–104.
- [10] Izaguirre A, Lanas J, Alvarez JI. Aging of lime mortars with admixtures: durability and strength assessment. Cem Concr Res 2010;40:1081–95.
- [11] Baronio G, Binda L, Lombardini N. The role of brick pebbles and dust in conglomerates based on hydrated lime and crushed bricks. Constr Build Mater 1997;11(1):34–40.
- [12] Baronio G, Binda L. Study of the pozzolanicity of some bricks and clays. Constr Build Mater 1997;11(1):41–6.
- [13] Papayianni I. The longevity of old mortars. Appl Phys A-Mater 2006;83:685–8.[14] Papayianni I, Stefanidou M. Durability aspects of ancient mortars of the
- archeological site of Olynthos. J Cult Her 2007;8:193–6.
- [15] Khatib JM, Wild S. Sulphate resistance of metakaolin mortar. Cem Concr Res 1998;28(1):83–92.
- [16] Malhotra SK, Dave NG. Investigations into the effect of addition of fly ash and burnt clay pozzolana on certain engineering properties of cement composites. Cem Concr Compos 1999;21:285–91.
- [17] Sabir BB, Wild S, Bai J. Metakaolin and calcined clays as pozzolans for concrete: a review. Cem Concr Compos 2001;23:441–54.
- [18] Blanco F, Garcia MP, Ayala J, Mayoral G, Garcia MA. The effect of mechanically and chemically activated fly ashes on mortars properties. Fuel 2006;85:2018–26.
- [19] Al-Akhras NM. Durability of metakaolin concrete to sulfate attack. Cem Concr Res 2006;36:1727–34.
- [20] Siddique R, Klaus J. Influence of metakaolin on the properties of mortar and concrete: a review. Appl Clay Sci 2009;43:392–400.
- [21] Lanzón M, García-Ruiz PA. Lightweight cement mortars: advantages nand inconveniences of expanded perlite and its influence on fresh and hardened state and durability. Constr Build Mater 2008;22:1798–806.
- [22] Topçu IB, Isikdag B. Manufacture of high conductivity resistant clay bricks containing perlite. Build Environ 2007;42:3540–6.
- [23] Patural L, Marchal P, Govin A, Grosseau P, Ruot B, Devès O. Cellulose ethers influence on water retention and consistency in cement-based mortars. Cem Concr Res 2011;41:46–55.
- [24] Kwan AKH, Wong HHC. Effects of packing density, excess water and solid surface area on flowability of cement paste. Adv Cem Res 2008;20(1):1-11.
- [25] EN 459-1. Building lime. Part 1: Definitions, specifications and conformity criteria; 2001.
- [26] ASTM C618-08. Standard Specification for coal fly ash and raw or calcined natural pozzolan for use in concrete. Annual Book of ASTM Standard, 4.02; 2008.
- [27] EN 1015-3. Methods of test for mortar for masonry Part 3: Determination of consistence of fresh mortar (by flow table); 1999.

- [28] EN 1015-11. Methods of test for mortar for masonry. Part 11: Determination of flexural and compressive strength of hardened mortar; 1999.
- [29] Martín Ramos JD. XPowder. A software package for powder X-ray diffraction analysis. Lgl. Dep. GR 1001/04; 2004.
- [30] Cizer O. Competition between carbonation and hydration on the hardening of calcium hydroxide and calcium silicate binders. PhD thesis. Katholieke Universiteit Leuven; 2009.
- [31] Matschei T, Lothenbach B, Glasser FP. The role of calcium carbonate in cement hydration. Cem Concr Res 2007;37:551–8.
- [32] De Silva PS, Glasser FP. Phase relations in the system CaO-Al₂O₃-SiO₂-H₂O relevant to metakaolin-calcium hydroxide hydration. Cem Concr Res 1993;23:627–39.
- [33] Rojas MF, Cabrera J. The effect of temperature on the hydration rate and stability of the hydration phases of metakaolin–lime-water systems. Cem Concr Res 2002;32:133–8.
- [34] Saikia N, Kato S, Kojima T. Thermogravimetric investigation on the chloride binding behaviour of MK-lime paste. Thermochim Acta 2006;444:16–25.

- [35] Frías M, Cabrera J. Pore size distribution and degree of hydration of metakaolin-cement pastes. Cem Concr Res 2000;30:561–9.
- [36] Arandigoyen M, Pérez Bernal JL, Bello López MA, Alvarez JI. Lime-pastes with different kneading water: pore structure and capillary porosity. Appl Surf Sci 2005;252:1449–59.
- [37] Pandey SP, Sharma RL. The influence of mineral additives on the strength and porosity of OPC mortar. Cem Concr Res 2000;30:19–23.
- [38] Lanas J, Alvarez JI. Masonry repair lime-based mortars: factors affecting the mechanical behaviour. Cem Concr Res 2003;33:1867–76.
- [39] Lanas J, Sirera R, Alvarez JI. Study of the mechanical behaviour of masonry repair lime-based mortars cured and exposed under different conditions. Cem Concr Res 2006;36:961–70.
- [40] Arizzi A, Martínez-Martínez J, Cultrone G, Benavente D. Mechanical evolution of lime mortars during the carbonation process. Key Eng Mater 2011;465:483–6.
- [41] Wild S, Khatib JM, Jones A. Relative strength, pozzolanic activity and cement hydration in superplasticised metakaolin concrete. Cem Concr Res 1996;26(10):1537–44.