



Research Paper

Properties of lime–metakaolin mortars for the restoration of historic masonries

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ABSTRACT

Mortars were prepared by mixing metakaolin/hydrated lime (with a ratio of ≤ 1 by mass) with sand and were evaluated in order to be used as restoration mortars on historic masonries. During 12-months curing time the chemical reactions were evaluated by thermal analysis (DTA/TG), the microstructural properties by mercury intrusion porosimetry (MIP) and the mechanical characteristics (flexural and compressive strength, static modulus of elasticity) by conventional mechanical tests. As the metakaolin/lime ratio increased, the content of total bound water, the static modulus of elasticity, the compressive and flexural strength increased while the pore size distribution shifted to smaller values. All mixes presented sufficient mechanical and microstructural properties comparable to traditional structural materials.

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1. Introduction

The masonry walls of historic buildings are degraded, depending on the traditional building materials (stones, bricks, aerial or hydraulic mortars, etc.), the specific environmental loads and the improper materials used in previous restoration interventions (cement, polymeric materials, etc.). Therefore, the restoration of masonry walls is indispensable after several years time. Through the centuries, historic mortars have proved to be long lasting and to be well compatible with the historic structural units. Therefore, the design of restoration materials should be approached by simulating the historic materials (Moropoulou, 2000; Papayianni, 2006).

Lime mixed with pozzolanic additions (natural and artificial) has been used extensively in the past as mortars for the construction of historic and traditional buildings (Bakolas et al., 1995; Giua, 1958). The use of high reactive pozzolans as an addition to lime mortars produce mortars, similar to historic ones, that exhibit an advanced durability to severe climate and moisture conditions and high values of mechanical strength (aqueducts, thermal baths, foundations of buildings, bridges, etc.) (Bakolas et al., 2008; Baronio and Binda, 1997).

Two types of pozzolans have been used in the past: natural, usually of volcanic origin and artificial like ceramic powder (Baronio and Binda, 1986; Moropoulou et al., 1995). Another artificial pozzolana that has been used in the past is metakaolin. In the literature is referred that lime–metakaolin mixes have been used to produce some Genoese white plasters and mortars of high durability called ‘porcellana’ (Chiaverini,

2004; Mannoni, 1988). These materials have been applied to the medieval port of Genoa construction (XV sec.) and, until now, present an excellent conservation state and a high adhesion of matrix to aggregates and substrate layer.

Metakaolinite is a highly active aluminosilicate which is formed by the dehydroxylation of kaolinite at ~ 650 – 800 °C temperature range. Many studies were published on the use of metakaolin (MK) as a pozzolanic additive to cement mortars and concrete (Frias and Cabrera, 2000; Frías Rojas and Sánchez de Rojas, 2005; Khatib and Wild, 1996; Sabir et al., 2001; Siddique and Klaus, 2009), the reaction kinetics of MK/cement (Frias and Cabrera, 2001; Frías Rojas and Sanchez de Rojas, 2003) and MK/lime (Bakolas et al., 2006; Cabrera and Frías, 2001; Cara et al., 2006; Morsy, 2005). Few studies considered the physico-mechanical and/or chemical properties of lime/metakaolin mortars and plasters (Bokan Bosiljkov, 2001; Fortes-Revilla et al., 2006; Rosario Veiga et al., 2009; Sepulcre-Aguilar, F. Hernandez-Olivares, 2010). These mixtures had been made with different materials, mixed with different proportions and curing conditions and were evaluated at early ages. Thus, the characteristics of these materials are very difficult to compare.

In this study metakaolin/lime mortars were prepared with different mix proportions. Their chemical and physico-mechanical properties were evaluated in order to use these materials as restoration mortars on historic masonries.

2. Experimental

2.1. Materials

Four mortars were prepared, by mixing metakaolin (MK)–Metastar 501 (Imerys) with commercial hydrated lime powder (L) (CaO Hellas)

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Table 1
Chemical analysis (XRF results in mass%) and physical properties of lime (L) and metakaolin (MK) used in mortars preparation.

	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	K ₂ O	Na ₂ O	SO ₃	LOI	dapp. g/cm ³	As m ² /g
L	0.17	0.18	0.07	70.06	2.35	–	–	0.77	25.60	0.50	13.6
MK	51.70	40.60	0.64	0.71	0.96	2.00	0.31	0.10	1.19	0.38	13.8

LOI: Loss of ignition; dapp.: apparent density according to EN-45; As: specific BET surface area.

at different MK/lime ratios. Table 1 reports the chemical composition and the physical properties of the materials used. In case of hydrated lime, DTA-TG indicated Ca(OH)₂ and CaCO₃ contents up to 89% and 6%, respectively.

Metakaolin presented a fine grain size distribution (cumulative value passing from 24 μm, 100%, and from 16 μm, 95.6%) as estimated by the laser particle size analyzer (CILAS 715). X-ray diffraction analysis revealed that the major mineral phases of metakaolin were mica, quartz and feldspar. Regarding the pozzolanic activity of MK, the total silica and active silica contents (according to EN 197-1 and EN 196-2) were determined as 54% and 45%, correspondingly. The pozzolanic activity of metakaolin (according to Hellenic Presidential Decree 244/1980, article 8) was determined as 13.1 MPa. The sand (Sq) was quartz standard sand (EN 196-1) with grain sizes in the range of 0–2 mm.

Table 2 reports the mortar mixes. The content (%) of sand was always 70 (mass%). The materials used were stirred with the appropriate amount of water for 15 min. This amount of water was chosen to reach the same consistence (EN 1015-Part 3). All mixes showed consistence of 15.7–15.8 cm (Table 2). The characteristics of fresh mortars were determined (Table 2) according to EN 1015. The retained water was 88%–90%, the bulk density was 1.85–1.90 g/cm³ and the air content varied between 2.5%–3.0%.

The mixes were casted in prismatic molds of 4×4×16 cm and in cylindrical molds of 4×8 cm for the mechanical strength and the static modulus of elasticity evaluation, respectively. All mortars were stored in a curing chamber with a relative humidity of 95±5% at 20±2 °C for the first 3 days after their preparation. They were then cured in a standard conditions chamber at the same temperature, at the humidity of 65±5%, till the testing date. MK1 and MK05 specimens were demolded the third day while the MK5 and MK2.5 mixes were demolded the seventh day.

2.2. Techniques

The following techniques were used to evaluate the mortars properties:

- Thermal analysis (DTA/TG—Netzsch 409EP) in a static air atmosphere with a heating rate of 10 °C/min from ambient temperature up to 1000 °C, in order to investigate the Ca(OH)₂ consumption and to determine the pozzolanic reaction products at different ages. DTA/TG measurements were performed before starting the curing period and after 1, 3, 6 and 12 months.
- Mercury intrusion porosimetry (MIP, Fisons, Porosimeter 2000) to evaluate the microstructural properties (cumulative volume, specific surface area, average pore radius, bulk density and open porosity) at 1, 3, 6 and 12 months of curing time.

Table 2
Mortar mixes (composition in mass%) and properties of fresh mortars.

Mix	Material (mass%)				dapp. g/cm ³	W _{ret.} (%)	Air (%)	Cons. (cm)
	L	MK	Sq	W/ (L+MK)				
MK1	15	15	70	0.96	1.85	88.2	3.0	15.8
MK05	20	10	70	0.92	1.86	88.4	2.6	15.7
MK5	25	5	70	0.81	1.90	89.0	2.5	15.8
MK2.5	27.5	2.5	70	0.79	1.90	90.4	2.6	15.7

W/(L+MK): water to lime plus metakaolin ratio (mass%); dapp.: apparent density; W_{ret.}: retained water; Air: air content; Cons.: consistence by flow table.

- Mechanical tests for the determination of mortars flexural and compressive strength at 1, 3, 6, 12 months (EN1015-11). The techniques used were ToniTechnik DKD-K-23301 for the compressive test (load rate: 0.01 kN/s) and a ToniTechnik-D-70804 for the flexural test (load rate: 0.05 kN/s). The static modulus of elasticity in compression testing was determined at 12 months of curing, by using the Wykeham Farrance test machine (max load: 50 kN, load rate: 0.1 mm/min).

3. Results and discussion

3.1. Thermal analysis

The main endothermic (endo) and exothermic (exo) peaks (Fig. 1) were detected at the following temperatures:

- ~105–120 °C (endo) dehydration of CSH
- ~180–200 °C (endo) dehydration of C₂ASH₈ (strätlingite or gehlenite hydrate) and C₃ACcH₁₁ (3CaO·Al₂O₃·CaCO₃·11H₂O, monocarboaluminate) (Bakolas et al., 2006)
- ~480–500 °C (endo) dehydration of Ca(OH)₂ (CH)
- ~575 °C (endo) phase transformation of unreacted quartz
- ~800 °C (endo) decomposition of CaCO₃

The peak related to the dehydration of CSH was firstly detected at 1 month and was sharper at 3 months whereas the intensity decreased at longer times. The endothermic peak at 180–200 °C could be attributed to both strätlingite and monocarboaluminate dehydration as these compounds were dehydrated at similar temperatures (Bakolas et al., 2006). The intensity of this peak remained rather stable from 1 to 6 months. The peaks attributed to CSH, strätlingite and monocarboaluminate dehydration were broadened at 12 months of curing time. The curves for the MK/lime mortars differed from those of MK/lime pastes (Bakolas et al., 2006). This phenomenon could be ascribed to the different storing conditions, the different dimensions of specimens and the presence of sand in the case of mortars.

The intensity of the endotherm CH dehydration decreased with time. At 12 months of curing time, a peak of CH was not detected. The endothermic reaction at 570 °C was related to the phase transformation of quartz. A significant peak related to CaCO₃ decarbonation was not observed from 1 to 6 months, only at 12 months a broad peak was detected at ~800 °C due to carbonation of the hydrated lime remaining after the completion of the pozzolanic reaction.

A similar trend was observed in the case of MK1 with higher intensities of the peaks related to the pozzolanic reaction products. MK5 and MK2.5 showed broader peaks with lower intensity while the peaks, related to CH dehydration and CaCO₃ decomposition, were sharper with higher intensity. This fact was attributed to the lower content of

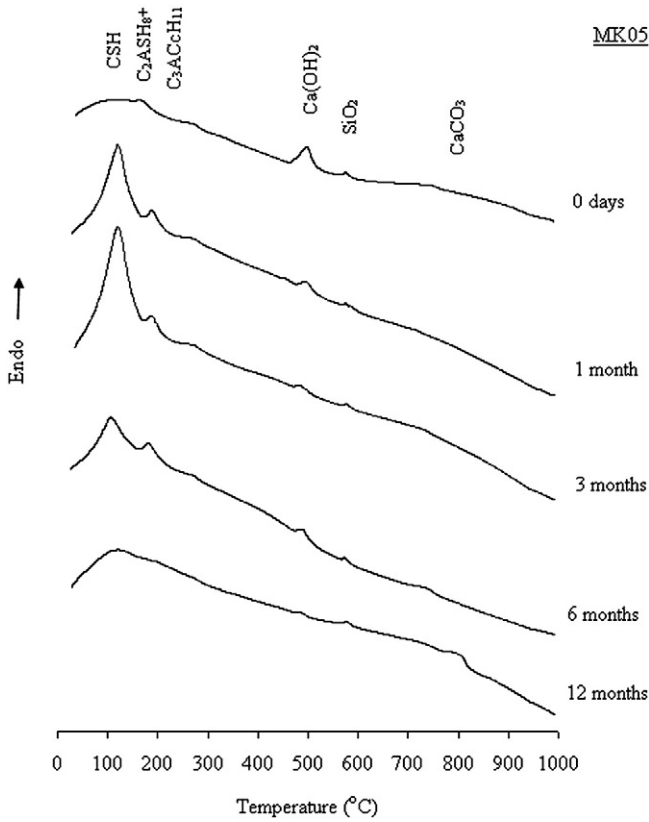


Fig. 1. DTA curves for MK05 at different curing times.

metakaolin in these mixes so that the amount of CH was not consumed by the metakaolin. Using TG/DTG analysis and the 2nd derivative of the DTA curves (Klimesch and Ray, 1997) the mass loss of the components were calculated (Table 3). The mass loss was attributed to

- total bound water ((H)_{tb}), calculated in the temperature range ~100–460 °C (Bakolas et al., 2006; Klimesch and Ray, 1997) according to the equation:

$$(H)_{tb} = (H)_{CSH} + (H)_{str+mca} + (H)_{rb}$$

where:

- (H)_{CSH}: bound water of CSH at ~100–160 °C
- (H)_{str+mca}: bound water of strätlingite and monocarboaluminate at ~160–230 °C
- (H)_{rb}: residual bound water at ~230–460 °C

- CO₂ release from CaCO₃

As the ratio MK/lime increased, the mass loss attributed to (H)_{tb} increased while the mass loss attributed to CaCO₃ decomposition de-

Table 3
Mass loss (%) of the components of the MK/lime mixes.

Mix design	Product	3 days	1 months	3 months	6 months	12 months
MK1	(H) _{tb}	5.49	16.37	13.31	11.70	5.27
	(CO) ₂	1.16	1.07	1.04	1.46	2.14
MK05	(H) _{tb}	3.46	11.95	14.67	8.75	5.38
	(CO) ₂	0.98	1.24	1.55	1.99	4.85
MK5	(H) _{tb}	1.86	4.85	3.24	3.67	3.60
	(CO) ₂	2.73	2.81	2.88	7.67	10.70
MK2.5	(H) _{tb}	0.93	2.44	2.44	2.20	1.91
	(CO) ₂	3.66	3.91	6.90	8.50	12.38

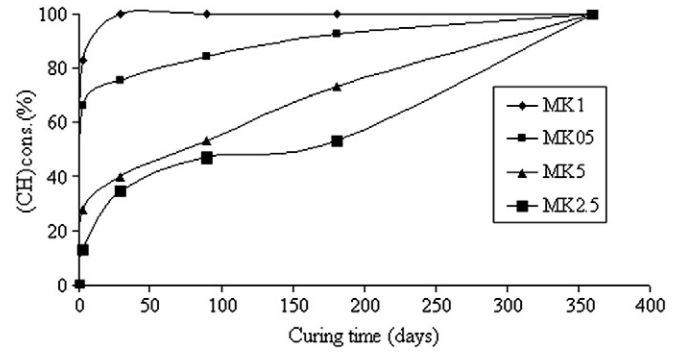


Fig. 2. Consumed CH for MK/lime at different ages.

creased. The maximum value of (H)_{tb} was found for the period of 1 to 3 months for all mixes. The decrease after 3 months was much steeper at higher metakaolin contents.

The mass loss due the CaCO₃ decomposition continuously increased with time for all mixes. These values were higher at higher hydrated lime contents in the initial mixes. The maximum value was found for MK2.5 (12.4% at 12 months).

Taking into account the TG results, the content of consumed Ca (OH)₂ ((CH)_{cons.}(%)) at a specific age (t) was determined according to the equation (Bakolas et al., 2006; Paya et al., 2003):

$$(CH)_{(cons.)}(\%) = 100 \cdot \frac{(CH)_0 - (CH)_t}{(CH)_0}$$

where:

- (CH)₀: initial amount of CH in the lime–metakaolin paste
- (CH)_t: amount of CH in the paste at a specific age (t)

Fig. 2 presents (CH)_(cons.)(%) versus the curing time for all mixes. The free CH of MK1 was consumed at 1 month whereas for the other mixtures free lime was not detected after 12 months. The CH consumption rate was increased as MK1 > MK05 > MK5 > MK2.5. As the content of MK was higher, larger amounts of hydrated lime reacted with metakaolin.

Table 4
Microstructure properties at different ages (mercury intrusion porosimetry data).

Mix	Curing time (months)	CV (mm ³ /g)	As (m ² /g)	PR (µm)	dbulk (g/cm ³)	TP (%)
MK1	1	167.04	18.24	0.03	1.69	28.23
	3	156.84	16.59	0.02	1.72	26.98
	6	205.93	21.91	0.03	1.65	33.98
	12	222.96	18.06	0.03	1.63	36.22
MK05	1	180.54	14.68	0.04	1.73	31.13
	3	168.81	8.12	0.05	1.76	29.71
	6	208.98	14.83	0.03	1.64	34.34
	12	235.81	10.41	0.04	1.60	37.46
MK5	1	183.34	9.76	0.24	1.70	31.17
	3	200.26	9.58	0.25	1.67	33.37
	6	207.55	8.59	0.25	1.67	34.58
	12	199.26	7.11	0.27	1.73	34.47
MK2.5	1	206.71	7.09	0.31	1.65	34.10
	3	213.73	5.89	0.31	1.64	35.11
	6	217.27	5.87	0.30	1.65	35.76
	12	207.34	5.34	0.31	1.70	35.25

CV: cumulative volume; As: specific surface area; PR: average pore radius; dbulk: bulk density; TP: total porosity.

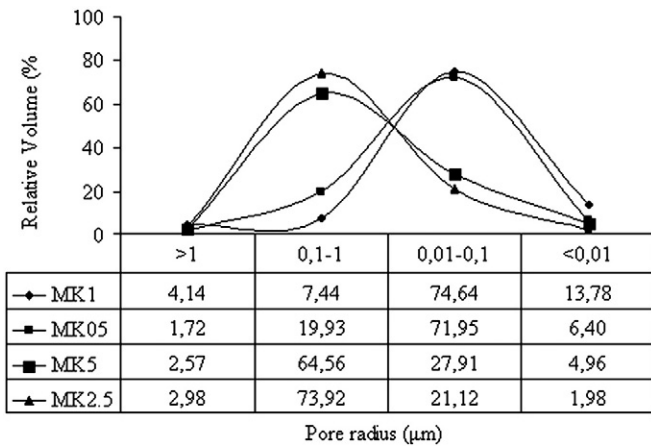


Fig. 3. Pore size distribution at 12 months curing time.

3.2. Mercury intrusion porosimetry (MIP)

Regarding the microstructural properties, two groups of mortars can be distinguished (Table 4). The first comprises MK1 and MK05 where the content of metakaolin was high (MK/lime = 1 and 0.5). For these mixtures the cumulative volume (CV) and the open porosity (OP) decreased from 1 to 3 months of curing and increased beyond this period. As expected, the bulk density showed an inverse trend. The average pore radius (PR) remained rather stable during the overall curing period. The specific surface area (As) fluctuated and at 12 months the higher value of As corresponded to the lower value of the average pore radius.

Regarding the second group (MK5 and MK2.5) CV value increased from 1 to 6 months, then decreased. Concerning the open porosity there was a slight increasing trend in time. The specific surface area decreased while average pore radius remained almost constant. The average pore radius for MK5 and MK2.5 were higher than MK1 and MK05. Bulk density fluctuated with the curing time: at 12 months the density was higher than the initial value due to the conversion of calcium hydroxide to calcium carbonate.

Fig. 3 reports the pore size distribution showing different distributions of the two groups of mortars. In the first group, there was a clear shift in the distribution to narrower pores, MK1 and MK05 had 88% and 78% of pore radii <0.1 μm. The cumulative curve of specific volume for MK1 increased, probably due to pores <0.0037 μm which could not be detected by the instrument. The range of microstructural parameters of the mixtures was similar to historic lime–pozzolan mortars (Moropoulou and Bakolas, 1998).

The distribution of the second group revealed larger pores. For MK5 and MK2.5 67% and 77% of the pore radii were >0.1 μm. This pore size

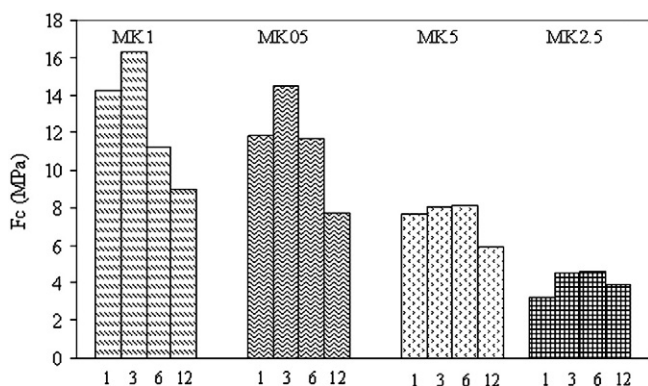


Fig. 4. Compressive strength of MK/lime mixes at different curing times.

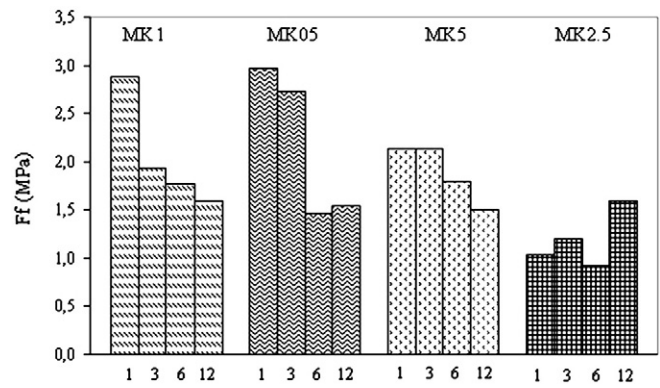


Fig. 5. Flexural strength of MK/lime mixes at different curing times.

distribution corresponded to that of lime mortars (Moropoulou et al., 2005a, 2005b).

3.3. Mechanical tests

The compressive strength of MK1 and MK05 showed a maximum value at 3 months of curing time (Figs. 4 and 5). Between 3 and 12 months the compressive strength decreased, a fact that was also detected by other authors (Chiaverini, 2004; Velosa et al., 2009). The reasons are unclear; microcracking due to shrinkage may play a role (Velosa et al., 2009). The compressive strength of MK5 was almost constant during the period 1–6 months (~8 MPa), then decreased to ~6 MPa at 12 months.

MK2.5 showed almost the same compressive strength value (3.2 MPa) at 1 and at 12 months (3.9 MPa). This more stable behavior was attributed to the use of higher contents (%) of lime in the mix. One should note that by mixing lime with a small content (2.5%) of a high reactive pozzolanic additive, like metakaolin, sufficient strength for restoration mortar was reached after 1 month as it can be observed for MK2.5 (Moropoulou et al., 2003). The final compressive strength increased with the ratio of MK/lime. The highest final value, at 12 months of curing, was found for MK1 (~9 MPa), followed by MK05 (~8 MPa), MK5 (~6 MPa) and MK2.5 (~4 MPa). The compressive strength did not change at 24 months of curing.

MK1, MK05, MK5 presented the maximum flexural strength at 1 month. This behavior may be attributed to the presence of microcracks due to the shrinkage, which strongly influences the flexural strength (Velosa et al., 2009). On the contrary, for MK2.5 the flexural strength was increasing with time.

Concerning the final values, all mixes exhibited almost the same flexural strength of 1.5–1.6 MPa. The flexural strength did not change within 12–24 months of curing.

The static modulus of elasticity for the MK/lime mixtures showed a similar trend with the compressive strength. MK1 presented the maximum value (451 MPa) and MK2.5 the lowest modulus (300 MPa) (Table 5). In general, all mortars presented low values of the elastic modulus, probably due to microcracking during shrinkage.

Table 5

Static modulus of elasticity for MK/lime mixes at 12 months of curing time.

Mix	Est. (MPa)	
	Aver.	SD
MK1	451	31
MK05	382	19
MK5	336	23
MK2.5	300	27

Est: static modulus of elasticity; Aver: average value of three measurements; SD: standard deviation.

4. Conclusions

The MK/lime mortars described in this study presented mechanical strength values which are needed in the restoration of historic masonries. All mixtures revealed mechanical and microstructural properties comparable to traditional structural materials.

As the ratio MK/lime increased in the mixtures, the mass loss attributed to total bound water of the pozzolanic reaction compounds increased and the mortars exhibited a clear shift in the pore size distributions to narrower pores ($<0.1 \mu\text{m}$).

The mechanical strength of mortars obtained a maximum value within 1–3 months of curing and it decreased till 12 months where the strength became stable. This loss of mechanical strength could be linked to microcracking due to shrinkage and it increased with the ratio of MK/lime.

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