

Strength development and lime reaction in mortars for repairing historic masonries

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Abstract

In this research, restoration mortars with analogous chemical composition of binders, aggregates and mineral additions, as they derive from the study of historic mortars, were evaluated regarding the strength development and the lime reaction, up to 15 months of curing. For this purpose several mixtures were tested in laboratory regarding their chemical and mechanical characteristics. The obtained results show that most of them present a slow rate of chemical and mechanical evolution, with the exception of hydraulic lime mortar and mortar with lime putty–natural pozzolanic addition. The best mechanical behavior was observed in mortars with lime powder and lime powder–artificial pozzolanic addition. These materials present also a low ratio of compressive to flexural strength (f_c/f_f). Further investigations on these materials would determine the time where their chemical and mechanical characteristics become stable. Only at that time, it would be possible to compare the compatibility characteristics of the restoration mortars with those employed in the past.

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1. Introduction

The masonry walls of historic buildings are degraded, depending on the traditional building materials (stones, bricks, aerial, pozzolanic or hydraulic mortars, etc.), the specific environmental loads and the materials used in previous restoration interventions (lime, gypsum, hydraulic lime, cement, polymeric materials, etc.). The degradation causes could be physical-related to physical variations of water inside masonry (evaporation, capillary flow, ice formation, etc.) or chemical (sulphate attack, alkali–silica reaction, formation of expansive products such as ettringite and thaumasite). In particular, ettringite and thaumasite, these high molecular weight compounds produced by the reaction of gypsum with the calcium aluminosilicates hydrates, provoke cracks and fissures in the mortar mass, due to the generation of high expansive stresses, in the case of ettringite and rend the mortar incoherent and without resistance in the case of thaumasite [1].

Therefore, the restoration of masonry walls is indispensable after several years of time. Taking into account that through the centuries historic mortars have proved to be well compatible with the historic structural units and long lasting under severe mechanical and environmental loads, the design of restoration materials should be approached by simulating the historic materials. However, during the last decades the industrial production of building materials has changed significantly. Traditional building materials and techniques have been replaced by cement technology, which displaced traditional binding materials resulting to the loss of traditional practice and building empiricism. Recent restoration interventions provoke significant failures and damage accelerations to the authentic building materials and structural units. The above negative results, as being mentioned in the literature [2,3], lead to the conclusion that cement-based materials are improper and incompatible with the historic building units [4]. Therefore, there is a demand for proper restoration mortars and building materials compatible with the original structures.

However, the term compatibility is not yet clearly clarified. There is a need for a precise definition of

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compatibility as far as traditional structures are concerned [5]. Up to now, the compatibility evaluation used to be based on experimental results at laboratory conditions, which differ significantly from the real ones and therefore they cannot be considered a safe and reliable way of estimating the compatibility of such composite systems. Materials cured and tested at laboratory conditions according to the cement practice within few months (usually until the 3rd month) are compared with authentic materials, which have exhibited longevity over centuries on masonries. These type of materials present slow rates of setting and hardening which have not been exactly determined till now. This is a principal factor that is not usually taken into account.

In this research, restoration mortars with analogous chemical composition of binders, aggregates and mineral additions, as they derive from the study of historic mortars [6], were evaluated regarding the strength development and the lime reaction in time. For this purpose several mixtures were tested in laboratory regarding their chemical and mechanical characteristics. Moreover, an attempt was made to estimate the curing time needed for the acquisition of maximum strength and the physico-chemical stability of the composite systems.

2. Materials and methods

For the production of mortars various materials were employed. Lime putty, lime powder and natural hydraulic lime were used as binding materials. Lime

putty is generally encountered in historic mortars [7,8], while lime powder was used as an alternative binding material for the substitution of lime putty due to the higher and quasi-stable percentage of $\text{Ca}(\text{OH})_2$ content. The aggregate materials were prevalently siliceous sand and crushed brick. The former has already been detected in historic mortar samples with the effect of producing lightweight mortars, due to its lower bulk density in respect to the sand aggregates, along with lower modulus of elasticity that it provides [9]. In some of the mixtures natural and artificial pozzolanic additions (Earth of Milos, Ceramic Powder respectively) were used. The ratio of binder/aggregates ranges between 1/1.5 and 1/3, while binder/pozzolanic additive ratio was 1/1 [10]. The characteristics of the above materials are reported in Table 1.

During the preparation of the mixtures the characteristics of fresh mortars were determined, according to DIN 18555 [11]. The mixtures were prepared by adopting a water–binder ratio (w/b) in the range of 0.7–1.2, in order to obtain mortars with about the same consistency (15.5–17.0 cm). The retained water ranged between 76% and 93% and the bulk density was 1.70–1.95 g/cm³. Table 2 shows the weight ratios of the various components employed for manufacturing mortars.

The specimens were stored at a moist curing chamber of $90 \pm 1\%$ relative humidity and $20 \pm 1^\circ\text{C}$ [12,13] for the first two days after their preparation and afterwards they were continuously cured at standard conditions of $20 \pm 1^\circ\text{C}$ and $50 \pm 1\%$ RH for 15 months.

Tests on compressive and flexural strengths were carried out at the time of 1, 3, 9 and 15 months in order

Table 1
Characteristics of building materials

Materials	Characteristics
Lime putty	77.6% $\text{Ca}(\text{OH})_2$ –3.2% $\text{Mg}(\text{OH})_2$ –14.1% CaCO_3 58.5% free water content Matured for 8 years
Lime powder	87.66% $\text{Ca}(\text{OH})_2$ –5.63% CaCO_3 0.18% free water content
Natural hydraulic lime	38% $\text{Ca}(\text{OH})_2$ –27% CaCO_3 11% insoluble, 20% C_2S 0.4% C_3A , 0.4% C_2AS , 0.4% C_4AF 0.5% CaSO_4 , 0.75% MgO 0.12% K_2O , 0.04% Na_2O NHL2 according to CEN prEN 459-1
Earth of Milos (natural pozzolana)	Fineness: 0% retained at 75 μm Pozzolanicity test: 6.0 MPa
Brick powder (artificial pozzolana)	Fineness: 94% passive at 64 μm Pozzolanicity test: 6.2 MPa
Sand	Siliceous sand 0/1 mm (washed) Sand equivalent: 92%
Crushed brick	Ceramic aggregates 1/6 mm (water saturated)

Table 2

Weight ratios of the various components used in the mortar manufacture

Mortar	Ratios per weight
NHLA	NHL2:Aggregates ^a = 1:2.3
LPA	Lime putty:Aggregates = 1:1.5
LPoA	Lime powder:Aggregates = 1:1.8
LPMA	Lime putty:Earth of Milos:Aggregates = 1:1:2
LPCPA	Lime putty:Ceramic powder:Aggregates = 1:1:2
LPoCPA	Lime powder:Ceramic powder:Aggregates = 1:1:2

^a Aggregates: mixed sand (0–1 mm) and crushed brick (1–6 mm).

to evaluate mechanical properties of mortars [Toni-Technik DKD-K-23301 compressive tester/load rate: 0.01 kN/s, ToniTechnik-D-70804 flexural tester/load rate: 0.05 kN/s]. Differential thermal analysis and thermogravimetric analysis [DTA/TG, Netzsch 409EP], in a static air atmosphere with heating rate of 10 °C/min from 25–1000 °C was employed in order to investigate the evolution of binder conversion in 15 months. Measurements were carried out on the total sample and on the fraction smaller than 63 µm, which constitutes the binding materials [6].

3. Results and discussion

3.1. Strength

In Table 3 the results of mechanical tests at 1, 3, 9 and 15 months are reported. Additionally, standard deviations of the three measurements for flexural strength and of the six measurements for compressive strength have been calculated. Moreover, the progress of compressive and flexural strength from 1 to 15 months, for all the mortars, is shown in Figs. 1 and 2, respectively.

According to the reported results, hydraulic lime mortar (NHLA) acquires quasi-maximum strength within the first month, with no significant variations of compressive strength afterwards. Flexural strength presents an increase of approximately 24% from the first to 15 months of curing.

Lime mortars exhibit a different behavior in the evolution of mechanical strengths. Mortar with lime putty (LPA) presents a 126% and 88% increase of compressive and flexural strength respectively, while mortar with lime powder (LPoA) exhibits an overall compressive strength increase of 222%, which is much higher compared to the relative increase of LPA. Moreover, from 1–3 to 3–9 months it doubles its compressive strength, while flexural strength increases by 137%. Comparing the above-mentioned lime mortars it is clear that LPoA presents a better behavior than LPA and this can be, mainly, attributed to the higher binder content in this mortar [14]. LPoA almost triples compressive strength value, while LPA doubles the corre-

Table 3

Flexural and compressive strength of mortars

Mortar	Curing (month)	Flexural strength (MPa)	SD	Compressive strength (MPa)	SD
NHLA	1	0.63	0.13	3.05	0.17
	3	0.69	0.14	3.25	0.34
	9	0.62	0.11	2.53	0.13
	15	0.78	0.04	3.02	0.14
LPA	1	0.25	0.05	0.69	0.11
	3	0.46	0.04	0.97	0.08
	9	0.52	0.02	1.34	0.14
	15	0.47	0.09	1.56	0.18
LPoA	1	0.40	0.15	0.90	0.06
	3	0.54	0.20	1.18	0.04
	9	0.76	0.09	2.40	0.13
	15	0.95	0.11	2.90	0.01
LPMA	1	0.34	0.04	0.63	0.05
	3	0.41	0.05	1.13	0.08
	9	0.40	0.04	1.12	0.06
	15	0.50	0.04	1.15	0.07
LPCPA	1	0.37	0.02	0.84	0.13
	3	0.43	0.01	1.22	0.07
	9	0.46	0.04	1.23	0.12
	15	0.48	0.02	1.34	0.21
LPoCPA	1	0.38	0.14	1.37	0.17
	3	0.62	0.10	2.36	0.11
	9	1.03	0.12	4.36	0.27
	15	1.30	0.29	4.60	0.23

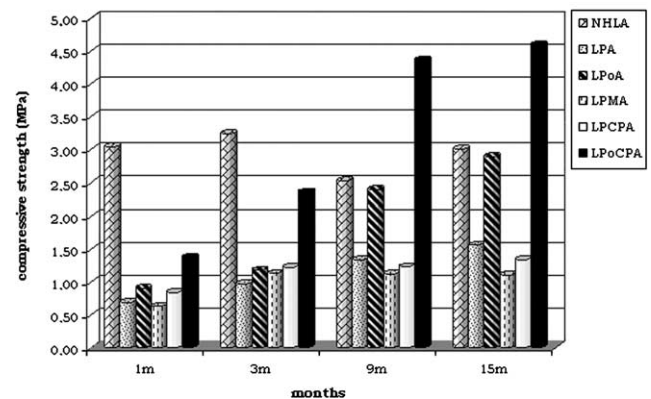


Fig. 1. Compressive strength of restoration mortars up to 15 months of hardening.

sponding value from 1 to 15 months of hardening. As far as flexural strength is concerned a slight variation was observed for LPA, while remarkable differences were detected for LPoA, as it over doubles its strength.

Mortars with pozzolanic additions (*natural* and *artificial*) and lime putty as binder acquire their maximum strength within 3 months. Mortar with natural pozzolanic addition (LPMA) presents a final increase of compressive and flexural strength of approximately 82% and 47% respectively. A similar behavior is exhibited by

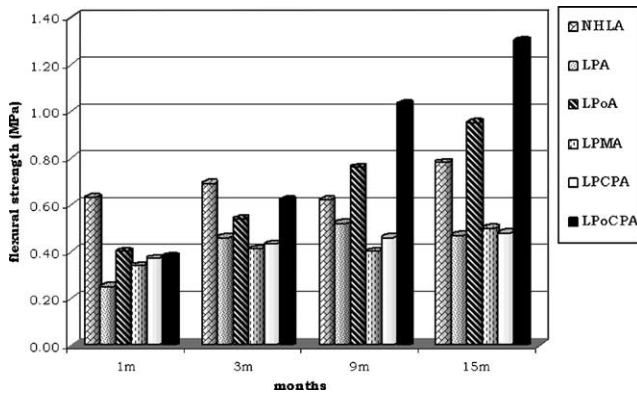


Fig. 2. Flexural strength of restoration mortars up to 15 months of hardening.

mortar with artificial pozzolanic addition (LPCPA). Nevertheless, the strength rate increase of these mortars is lower than the corresponding increase of pure lime mortars (LPA, LPoA). This fact indicates that these mortars show a mechanical behavior similar to that of the pure lime mortars. On the contrary, the mechanical behavior of mortar with lime powder and artificial pozzolanic addition (LPoCPCPA) differs significantly from that of the other pozzolanic mortars. It over triples compressive strength from 1 to 15 months with an increase of 236%, while flexural strength augments in the same way (242%). Moreover, a trend for further strength development can be observed over 15 months of curing for lime powder and lime powder–artificial pozzolanic addition as well.

However, all mortars present a low ratio of compressive to flexural strength (f_c/f_f), which suggests that those mortars are characterized by an elastic behavior compatible with that of the original ones. This fact is supported by a research carried out by Briccoli and Rovero [10]. These authors found that the ratio f_c/f_f of similar materials is proportional to the modulus of

elasticity (E), for mechanical measurements from 1 to 6 months. This research concludes that a low f_c/f_f ratio corresponds to a low modulus of elasticity, which was determined in the case of lime mortars [10]. This behavior could probably be attributed to the presence of lime and ceramic aggregates as well, that also produce lightweight mortars [8,9,15]. Furthermore, in order to accomplish the evaluation of mechanical behavior of restoration mortars in historic masonries, the elastic modulus should be determined.

3.2. Thermal analysis

Table 4 reports the results of DTA and TG expressed as weight percentage of the chemical compounds detected in mortar mixtures (mean value of three measurements). The DTA and TG tests were carried out on the total sample and on the mortar fraction smaller than 63 μm (binder). The initial content of $\text{Ca}(\text{OH})_2$ in the mortars was taken into account in order to estimate its conversion in time.

The amount of $\text{Ca}(\text{OH})_2$ in the samples is the principal factor for monitoring the chemical evolution of these composite systems in time. In all mortars $\text{Ca}(\text{OH})_2$ should be converted into CaCO_3 apart from pozzolanic mortars, where the carbonation reaction takes place concurrently with the pozzolanic reaction. The chemically bound water reported is ascribed not only to the formation of hydraulic compounds but also to the loss of chemically bound water of aggregates. In fact, some aggregates, as micas and other minerals, may contain an appreciable amount of chemically bound water [16].

From the results of DTA-TG analysis it can be observed that in NHLA and LPMA mortars there is no evidence of $\text{Ca}(\text{OH})_2$. For the above-mentioned mortar a 100% conversion of $\text{Ca}(\text{OH})_2$ can be noticed. This is mainly attributed to the carbonation, in the case of natural hydraulic lime mortar (NHLA), and to the

Table 4
TG analysis of the compounds (% per weight) presented in mortars after 15 months of curing

Mortar		Hygroscopic water	Chemically bound water	$\text{Mg}(\text{OH})_2$	$\text{Ca}(\text{OH})_2$	CaCO_3
LPA	Binder	0.58	1.87	2.56	20.74	66.09
	Total	0.26	0.53	0.81	4.61	20.33
LPoA	Binder	0.38	1.26	–	14.57	76.96
	Total	0.22	0.58	–	4.53	33.25
LPCPA	Binder	0.77	1.54	1.81	2.63	33.55
	Total	0.29	0.76	0.62	0.99	15.44
LPoCPCPA	Binder	0.79	2.26	–	6.30	47.19
	Total	0.49	1.28	–	2.68	11.80
LPMA	Binder	0.61	5.41	–	–	32.57
	Total	0.36	2.43	–	–	14.49
NHLA	Binder	1.24	3.28	–	–	68.61
	Total	0.62	1.21	–	–	23.93

carbonation and to the slight bound of Ca(OH)_2 from the aluminosilicate compounds in the case of lime putty–natural pozzolanic addition mortar. These results agree with the strength rate. The other mortars show slower strength rates, either chemically or mechanically. In fact these materials show the presence of Ca(OH)_2 even after 15 months of curing. In particular, mortar with lime powder and artificial pozzolanic addition exhibits an 85% conversion of Ca(OH)_2 in 15 months, while an amount of 6.3% Ca(OH)_2 remains unreacted. As mentioned in the literature [17], free Ca(OH)_2 is detected in historic mortars as a consequence of the factors that inhibits carbonation (high relative humidity environments, walls of great thickness, etc.). Since these factors do not influence the samples under examination, a further conversion of chemical compounds can be expected, as it can also be noticed from strength rate. Mortars with lime putty and artificial pozzolanic addition (LPCPA) exhibit a different chemical behavior compared with that with natural pozzolanic addition (LPMA). Both mortars present analogous mechanical behavior, but LPCPA seems to be still in evolution. This mortar presents unreacted Ca(OH)_2 and exhibits an 83% conversion, similar to the one with lime powder and artificial pozzolanic addition, although the last exhibits different mechanical behavior. According to the above results, the mortar with lime putty–natural pozzolanic addition (LPMA) evolves more rapidly with respect to that with artificial pozzolanic addition (LPCPA). This could be attributed to the different physical and chemical characteristics of these two pozzolanic additions.

Lime mortars show the largest amounts of unreacted Ca(OH)_2 . Mortar with lime putty exhibits a 73% conversion, while mortar with lime powder presents a higher conversion of about 84%. This behavior was unexpected, on the basis of the different initial amounts of Ca(OH)_2 in the two mortars. However, this difference could be ascribed to the different microstructural development and permeability factors that partially inhibit carbonation in lime putty mortar. The above results are confirmed by the strength rate, which exhibit a trend for further rise.

4. Conclusions

From the obtained results the following conclusive remarks can be point out:

- All the examined mortars present very slow rates of hardening, with the exception of hydraulic lime mortar (NHLA) and mortar with lime putty–natural pozzolanic addition. This fact is confirmed by the rate of mechanical evolution and from Ca(OH)_2 conversion. All mortars, except the above mentioned, seem to be in progress after 15 months of curing.

- The best mechanical behavior was observed in mortars with lime powder and lime powder–artificial pozzolanic addition. These materials present also a low ratio of compressive to flexural strength (f_c/f_f).
- Further investigations on these materials would clarify the kinetic of chemical evolution of the compounds and also the strength rate and the time at which these materials obtain their chemical and mechanical stability. Only at the stability time it would be possible to compare the compatibility characteristics of these restoration mortars with those employed in the past.
- Moreover, other factors such as elastic modulus and chemical interaction with materials of historic masonries should be investigated in order to evaluate the restoration mortars compatibility and behavior in historic masonries.

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