Physical and chemical assessment of lime-metakaolin mortars: Influence of binder:aggregate ratio

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Abstract

This work evaluates the influence of the binder:aggregate ratio in respect to mineralogical and mechanical properties of air lime-metakaolin mortars. Mineralogical analysis showed that binder:aggregate ratios modifies the extent of carbonation and pozzolanic reactions with curing. The pozzolanic reaction occurs mostly at lower curing times (28 days), while, at higher curing ages, carbonation reaction is mostly dominant. The exceptions are mortars with 1:1 (air:lime) volumetric ratio with 30\% and 50\% MK in which the pozzolanic reaction is still dominant. For conservation purposes, the mechanical tests demonstrated that 1:2 and 1:3 mortar volumetric ratios were considered adequate proportions since 1:1 was considered a “strong” ratio, as it can induce tensions and mortar shrinkage that can damage historic masonries.

Keywords

Air lime mortars; metakaolin; pozzolanic phases; XRD; TG-DTA; mechanical tests
Nomenclature

MK – metakaolin
$C_2ASH_8$ – stratlingite
$C_2AH_{6.5}$ – calcium aluminate hydrate
$CSH$ – calcium silicate hydrate
$CH$ – portlandite
$CaCO_3$ – calcite
$CO_2$ – carbon dioxide
$CaAl_{2}H_{11}$ – monocarboaluminate
$CSH$ – calcium silicate hydrate
XRF - X-Ray Fluorescence analysis
XRD – X-Ray Diffraction analysis
TG-DTA – Thermogravimetric and Differential Thermal Analysis
RH – relative humidity
Stdev – Standard deviation

1. Introduction

Since ancient times mortars were created and developed with traditional techniques using easily-available materials, by several civilizations [1]. Nowadays, awareness of the need for compatible materials regarding the preservation of the architectural heritage has resulted in the revival of lime-based mortar technology and applications [2,3,4]. However, several difficulties occur when using mortars solely of air lime, due to their inability to harden without contact with $CO_2$, to harden under water and their slow setting. Several studies demonstrated that lime-pozzolan blended mortars showed faster setting properties, as well as an increase of their durability [5-12].

Due to its high pozzolanic activity, metakaolin (MK) was used in this study for the formulation of the lime-pozzolan mortar system compositions in this study. Many
studies have been accomplished regarding the effects of MK additions to cement mortars in order to achieve strength and durability [6, 13-17]; however, only few and very recent studies about the reactions occurring in air lime-MK mortars and their influence towards historic masonry requirements have been made [18-20]. Also, very little attention has been given in terms of understanding the role of hydration and carbonation reactions in lime-MK mortars as well as their mechanical and chemical properties [21].

The principal objective of the present research was to seek the optimization of air lime-MK mortar composition for historical heritage purposes, by learning and understanding their chemical and physical properties. This study deals with the mineralogical and physical-mechanical variations produced in mortars when the binder is constituted by air lime and a metakaolin. Also, it is shown a comparison between mortars with and without added metakaolin. This research can be divided in two parts: first, air lime mortars with MK in different combinations with fixed binder:aggregate ratio; and secondly, mortars with fixed combination of mortar and MK with variation of the binder:aggregate ratio.

To accomplish this, three different volumetric binder:aggregate ratios of lime-MK blended mortars compositions with three different MK contents were prepared and submitted to curing conditions of 90±5% RH and a temperature of 20±3ºC. Several physical and chemical tests, namely flexural and compressive strength, X-ray diffraction analysis (XRD) and simultaneous thermogravimetric and differential thermal analysis (TG-DTA), were conducted focusing mainly on characterizing the evolution of the lime-MK mortars hardening in respect to time.

2. Materials and methods

Mortars with volumetric binder:aggregate ratios of 1:1, 1:2 and 1:3 were prepared by mixing a Portuguese powdered commercial air lime EN 459-1 [22] CL90-S (Lusical H100 - L) and a washed, well graded siliceous river sand, mainly composed of quartz
and some feldspar minerals. The lime binder content was maintained or replaced by 30% or 50% wt. of a commercial metakaolin (ARGICAL M1200S – MK), with specific surface area, by Blaine, of 3.38 m²/g and particle size distribution: d(10%)=1.53µm, d(50%)=4.35 µm and d(90%)=11.97 µm. The chemical composition (major elements) was carried out by X-ray fluorescence analysis (XRF) using a Panalytical Axios X-ray fluorescence spectrometer with CrKα radiation. Loss-on-ignition (LOI) was determined by sample calcination at 1000°C for 3 hours. Table 1 presents the chemical composition of the metakaolin and air lime used as binder in mortar production. The mortar mixes identification, volumetric and weight ratios, percentage of lime weight substitution by MK and water/binder ratio, are shown in Table 2.

Table 1 – Chemical composition (in wt. %) of materials used as binder in mortar preparation.

<table>
<thead>
<tr>
<th>Material</th>
<th>SiO₂</th>
<th>Al₂O₃</th>
<th>Fe₂O₃</th>
<th>MnO</th>
<th>MgO</th>
<th>CaO</th>
<th>Na₂O</th>
<th>K₂O</th>
<th>TiO₂</th>
<th>P₂O₅</th>
<th>L.O.I.*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Metakaolin</td>
<td>54.39</td>
<td>39.36</td>
<td>1.75</td>
<td>0.01</td>
<td>0.14</td>
<td>0.10</td>
<td>–</td>
<td>1.03</td>
<td>1.55</td>
<td>0.06</td>
<td>1.90</td>
</tr>
<tr>
<td>Air Lime</td>
<td>–</td>
<td>0.01</td>
<td>0.15</td>
<td>0.01</td>
<td>3.09</td>
<td>76.74</td>
<td>–</td>
<td>0.02</td>
<td>0.04</td>
<td>0.01</td>
<td>20.45</td>
</tr>
</tbody>
</table>

*Loss on ignition

Table 2 – Mortar mixes identification, volumetric and weight binder:aggregate ratio, MK replacement content, materials quantities, water/binder ratio and flow table consistency.

<table>
<thead>
<tr>
<th>Sample identification</th>
<th>Binder:Aggregate ratio</th>
<th>MK</th>
<th>Quantities (wt. %)</th>
<th>Water/Binder</th>
<th>Consistency [mm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>L1</td>
<td>1:1</td>
<td></td>
<td>Lime    MK Sand</td>
<td>(wt.)</td>
<td></td>
</tr>
<tr>
<td>L1MK30</td>
<td>1:1:4</td>
<td></td>
<td>0 20.54 0</td>
<td>79.46</td>
<td>1.1 140±1</td>
</tr>
<tr>
<td>L1MK50</td>
<td>1:1:4</td>
<td></td>
<td>30 14.38 6.16</td>
<td>138±2</td>
<td></td>
</tr>
<tr>
<td>L2</td>
<td>1:2</td>
<td></td>
<td>50 10.27 10.27</td>
<td></td>
<td></td>
</tr>
<tr>
<td>L2MK30</td>
<td>1:2:8</td>
<td></td>
<td>0 11.45 0</td>
<td>88.55</td>
<td>1.7 129±2</td>
</tr>
<tr>
<td>L2MK50</td>
<td>1:2:8</td>
<td></td>
<td>30 8.01 3.43</td>
<td>138±2</td>
<td></td>
</tr>
<tr>
<td>L3</td>
<td>1:3</td>
<td></td>
<td>50 5.72 5.72</td>
<td></td>
<td></td>
</tr>
<tr>
<td>L3MK30</td>
<td>1:3:12</td>
<td></td>
<td>0 7.93 0</td>
<td>92.07</td>
<td>2.5 143±5</td>
</tr>
<tr>
<td>L3MK50</td>
<td>1:3:12</td>
<td></td>
<td>30 5.55 2.38</td>
<td>139±5</td>
<td></td>
</tr>
</tbody>
</table>

2.1 Mortar preparation: mixing and curing procedure

The mixing procedure was the same for all mortars: the amount of water to achieve a comparable consistency, trying to correspond to an adequate workability for this kind of
mortars, was added in the first seconds of mixing; mechanical mixing went on for 150 seconds; the borders were scrapped and the mixing continue for another 30 seconds. The flow table consistency was determined based on EN 1015-3 [23]. Mortars were casted in metallic prismatic moulds of 40 x 40 x 160 mm and conditioned inside polyethylene bags during 6 days for initial curing with high RH. After removing the mortar samples from the moulds, they were maintained at a RH of 90±5% and 20±3°C temperature and cured up to ages of 28 and 90 days. Mortars without MK could not be demoulded at the 6th day of curing due to the fact that they were too soft to demould and needed to be left for one more day outside the bag to be demoulded. The day before initializing testing, samples were stored for 24h at 20±3°C and 65±5% RH in a climatic chamber.

2.2 Flexural and compressive strength tests

Mortar flexural strength was determined by the average of three points bedding strength of three mortar samples of each mortar, using an universal tensile machine Zwick Z050 with a 2 kN load cell and velocity of 0.2 mm/min, based on EN 1015-11 [24]. At 28 days the core of the samples, when fractured, still presented high moisture, particularly those of mortars with MK, showing a diverse behaviour at that lime-based mortars young age.

The same equipment but with a compressive device, a load cell of 50 kN and a velocity of 0.7 mm/min, was used for the compressive strength determination of each mortar, using half samples from the previous test, and also based on EN 1015-11 [24]. Remaining pieces of mortars from the compressive strength's test were dried at 60°C temperature and used for further mineralogical and thermal characterization.
2.3 X-ray diffraction analysis

The samples for XRD analysis were dried and sieved in order to enrich the mortar binder fraction. These samples were afterwards ground to granulometry < 106μm. X-ray diffractograms were obtained on a Philips PW3710 X-ray diffractometer, with 35 kV and 45 mA, using Fe-filtered CoKα radiation of wavelength λ=1.7903 Å. Diffractograms were recorded from 3-74 °2θ, in 0.05 °2θ increments with 1 second per increment, in effect 0.05 °2θs⁻¹.

2.4 Thermogravimetric and differential thermal analysis (TG-DTA)

The mortar samples to be analysed by TG-DTA were dried and ground to granulometry up to 106μm. The TG-DTA analysis was performed in a TG-DTA analyser, under argon atmosphere, with heating rate of 10ºC/min, from room temperature to 1000ºC. Free portlandite content in the samples was determined from the mass loss in the range of 380–500ºC, corresponding to portlandite dehydration region. The CO₂ content present in the samples was attained in the mass loss range of 500–850ºC, which corresponds to the decarbonation region of carbonates [25-28].

3. Results and analysis

3.1 Water/binder ratio and flexural and compressive strength

All the mortars presented an adequate workability for air lime based mortars. The average value of consistency for each mortar is presented in Table 2, with an average flow table consistency of 138 ± 5 mm for all the mortars.

Also, from Table 2 it is viewed that the water/binder ratio that was needed to achieve comparable consistency increases with the decrease of the binder:aggregate ratio and the extent of MK. Figure 1 and 2 presents flexural and compressive strength results of mortars, in terms of average and standard deviation of each three samples tested.
As expected, flexural strength decreases with the decrease of the binder:aggregate ratio of mortars. The decrease of flexural strength with the binder:aggregate ratio is even clearer at the age of 90 days compared with 28 days. For each binder:aggregate mortar ratio, the flexural strength increases with the wt. % of lime substitution by MK, except for L1MK50 at 28 days (highest Stdev test) and L3MK30 at 90 days. Also it
increases from 28 to 90 days of age, except for L1MK30 and for mortars L3 with MK. This reduction may be due to mortars shrinkage with microcracking, and also due to the increase of the water/binder ratio. Also, as expected, the mortars' compressive strength follows the behaviour of the flexural strength, decreasing with the binder:aggregate ratio. As previously, this decrease is also clearer at the age of 90 days. The compressive strength increases with the wt. % of lime substitution by MK for all mortars, which seem to be induced by the occurrence of a pozzolanic reaction. It increases from 28 to 90 days except for L1MK30 and for the L3MK mortars, following the behaviour shown by the flexural strength results and by the same probable reasons.

### 3.2 XRD results and analysis

The XRD results of 1:1, 1:2 and 1:3 mortars are displayed in Fig. 3. The patterns correspond to the binder rich fractions of the mortars. Also, a comparison of the evolution between 28 and 90 days of curing is shown. In these figures the bold arrows were drawn signalling the most intense peaks of the hydrated compounds originated in lime-MK reaction.
Fig. 3 – XRD patterns of binder rich fraction of mortars with (a) 1:1, (b) 1:2 and (c) 1:3 volumetric ratios, 28 days versus 90 days of curing.

Notation:
St – Stratlingite (2CaO·SiO₂·Al₂O₃·8H₂O);
M – Monocarboaluminate (3CaO·Al₂O₃·CaCO₃·11H₂O); CSH – Calcium silicate hydrate;
D – calcium aluminate hydrate (Ca₂Al(OH)₉·6.5H₂O); P – Portlandite (Ca(OH)₂);
C – Calcite (CaCO₃); Q – Quartz (SiO₂); F – Feldspar (KAlSi₃O₈); V – Vaterite (CaCO₃);
KA – Katoite (Ca₃Al₂(SiO₄)(OH)₈).

As viewed in Figure 3, the main phases formed in the pure air lime mortars (0% MK) at 28 and 90 days of curing are portlandite (CH) and calcite (C). As expected, the calcite content increases with curing age due to the evolution of carbonation reaction. Comparing Figure 3 (a), (b) and (c), calcite peaks are more intense for mortars with lower binder content, i.e., L2 and L3, also increasing with curing time (90 days). Also as
the presence of quartz and feldspar are also detected since they are constituents of the siliceous sand used in the mortars formulation.

Figure 3 (a), (b) and (c) also show that mortars prepared with MK (e.g. L1MK30 and L1MK50) present a steep decrease in the portlandite content with ageing, due to its consumption towards the pozzolanic hydration, as well as for the carbonation reaction. The hydrated phases obtained in the lime-MK reaction are stratlingite \((\text{Ca}_2\text{Al}_2\text{SiO}_{7.8}\text{H}_2\text{O} - C_2\text{ASH}_9)\), calcium aluminate hydrate \((\text{Ca}_2\text{Al(OH)}_{7.6.5}\text{H}_2\text{O} - C_2\text{AH}_{6.5})\) and monocarboaluminate \((\text{Ca}_4\text{Al}_2\text{O}_6\text{CO}_3\text{11H}_2\text{O} - \text{C}_4\text{A}\overline{3}\text{H}_{11})\). The monocarboaluminate, as described by Arrizi and Cultrone [18], derives from the reaction between the reactive alumina of MK and the free portlandite found in the mortars in the presence of \(\text{CO}_3^{2-}\). The monocarboaluminate occurs in higher intensity for L1MK30 at 28 days, decreasing with time and also with higher MK content. This decrease with MK content was also observed for the remaining lime-MK mortars. Calcium aluminum hydrate occurs in MK30 and, in a minor content, in MK50 mortars both at 28 days, decreasing with ageing. The two aluminate hydrated phases identified in MK mortars present an unstable behaviour with increasing curing age. This behaviour could be attributed, as described by Silva and Glasser [29], to the reduction of \(\text{Ca}^{2+}\) and \(\text{OH}^-\) ions in the pore solution.

In contrast, stratlingite, a hydrated compound normally responsible for the improvement of mechanical strength of lime-MK mortars [30, 31], increases with ageing and MK content. As can be seen at 28 days for MK30 mortars (Fig. 3), the stratlingite peaks presents similar intensity, with exception of L1MK30. However, at 90 days of curing the stratlingite peaks are present with similar intensity in all MK30 mortars. This behavior of stratlingite could indicate the ending of pozzolanic reaction at 90 days of ageing.

For MK50 mortars, it is observed an increase in the intensity of stratlingite peaks when compared with MK30 mortars. This seems to be caused by the increase in the pozzolanic reaction due to higher MK content. When comparing all MK50 mortars, the highest intensity of stratlingite is observed for L1MK50 mortar.
The relative higher importance of the unstable aluminate hydrated phases by comparison with the more stable stratlingite in all L3MK mortars and in L1MK30 mortar may also contribute to explain the decrease in flexural and compressive strength from 28 to 90 days in the referred mortars.

Calcite is also present in all mortars, showing a slight increase with curing age. Calcite content is higher for 1:3 mortars and, for those containing MK, it presents the highest content in mortars with 30% MK. This seems to be due to a less dense microstructure of mortars possessing weaker binder:aggregate ratios, lower MK content and also high water/binder ratio, which all together may favour quicker carbonation.

Figure 3 also shows the presence at 28 days in MK30 mortars of a low silica hydrogarnet – katoite (Ca$_3$Al$_2$(SiO$_4$)(OH)$_8$). Silva and Glasser [29], stated that mixtures containing stratlingite and calcium hydroxide are expected to form katoite, which is viewed to be a compound that carries out negative effects in MK blended mixes. However, the results at 90 days did not show any occurrence of this phase, which can be related with the decrease of CH.

3.3 TG-DTA results and analysis

Figures 4 and 5 presents the dTG charts for the mortars under analysis. These charts presents 3 main peaks in the temperature ranges of $T_{ambient}$-200ºC, 380-500ºC and 500-850ºC, corresponding to the pozzolanic product dehydration, portlandite dehydration and the carbonates decarbonation regions, respectively.
Fig. 4 – dTG results of L1, L1MK30, L2, L2MK30, L3 and L3MK30 mortars (28 and 90 days of curing), showing the characteristic regions for pozzolanic dehydration (CSH, $C_{2}ASH_{8}$, $C_{4}A\tilde{C}H_{11}$, $C_{2}AH_{6.5}$), portlandite (CH) dehydration and carbonates decarbonation.
Fig. 5 – dTG results of L1MK30, L1MK50, L2MK30, L2MK50, L3MK30 and L3MK50 mortars (28 and 90 days of curing), showing the characteristic regions for pozzolanic dehydration (CSH, C₂ASH₆, C₄AH₁₁, C₂AH₆,₅), portlandite (CH) dehydration and carbonates decarbonation.
Table 3 presents the mass losses (in %) obtained by TGA corresponding to the pozzolanic dehydration, portlandite dehydration and the carbonates decarbonation regions.

<table>
<thead>
<tr>
<th>Simple identification</th>
<th>Mass losses [%]</th>
<th></th>
<th></th>
<th>T&lt;sub&gt;amb&lt;/sub&gt;-200ºC</th>
<th>380-500ºC</th>
<th>500-850ºC</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>28 d</td>
<td>90 d</td>
<td>28 d</td>
<td>90 d</td>
<td>28 d</td>
<td>90 d</td>
</tr>
<tr>
<td>L1</td>
<td>0.34</td>
<td>0.59</td>
<td>3.03</td>
<td>0.78</td>
<td>1.89</td>
<td>9.07</td>
</tr>
<tr>
<td>L1MK30</td>
<td>3.69</td>
<td>3.58</td>
<td>0.84</td>
<td>0.83</td>
<td>1.56</td>
<td>2.09</td>
</tr>
<tr>
<td>L1MK50</td>
<td>4.77</td>
<td>4.42</td>
<td>0.38</td>
<td>0.39</td>
<td>1.70</td>
<td>1.62</td>
</tr>
<tr>
<td>L2</td>
<td>0.33</td>
<td>0.26</td>
<td>0.45</td>
<td>0.15</td>
<td>4.15</td>
<td>5.34</td>
</tr>
<tr>
<td>L2MK30</td>
<td>2.31</td>
<td>1.60</td>
<td>0.51</td>
<td>0.17</td>
<td>1.48</td>
<td>2.90</td>
</tr>
<tr>
<td>L2MK50</td>
<td>5.15</td>
<td>2.27</td>
<td>0.36</td>
<td>0.16</td>
<td>1.22</td>
<td>1.55</td>
</tr>
<tr>
<td>L3</td>
<td>0.12</td>
<td>0.18</td>
<td>0.46</td>
<td>0.19</td>
<td>1.53</td>
<td>2.45</td>
</tr>
<tr>
<td>L3MK30</td>
<td>1.37</td>
<td>1.19</td>
<td>0.23</td>
<td>0.16</td>
<td>1.19</td>
<td>1.81</td>
</tr>
<tr>
<td>L3MK50</td>
<td>1.59</td>
<td>1.74</td>
<td>0.17</td>
<td>0.15</td>
<td>1.06</td>
<td>1.05</td>
</tr>
</tbody>
</table>

From Figures 4 and 5 it can be seen that at 28 days of curing all lime and MK mortars show, with exception of the L3MK50 mortars, the presence of a peak at about 450ºC indicating the existence of free portlandite. Also, at about 750ºC, the existence of a peak confirms the presence of calcite, as pointed out in XRD section. At this age of curing, two other peaks can be also observed in all lime-MK mortars, but with higher incidence in MK50 mortars. The first one is at about 150ºC, corresponding to the dehydration of CSH and C<sub>2</sub>AH<sub>6.5</sub>, while the second one, at about 220ºC, is attributed to both C<sub>2</sub>A<sub>11</sub>H<sub>11</sub> and C<sub>2</sub>ASH<sub>8</sub> [19,30].

At 90 days of curing pozzolanic peaks are present for all MK mortars, being again more important for MK50 mortars. At this age the portlandite peak is also noticed for all mortars, with exception of all the MK50 mortars. In comparison with 28 days, the calcite peak is highest for all mortars at 90 days. This behaviour is confirmed by the XRD analysis.
3.3.1 Pozzolanic vs carbonation reaction evolution

Aiming to study the evolution of the pozzolanic reaction versus the carbonation reaction with mortars’ ageing, determination of consumed portlandite in pozzolanic and carbonation reactions was evaluated according to equations 1 and 3, respectively:

\[ CH_{poz} = CH_{th} - (CH_{f} + CH_{carb}) \]  

[Equation 1]

\[ CH_{f} = (ML_{(380-500^\circ C)}) \times \frac{MM(CH)}{MM(H_{2}O)} \]  

[Equation 2]

\[ CH_{carb} = (ML_{(500-850^\circ C)}) \times \frac{MM(CH)}{MM(CO_{2})} \]  

[Equation 3]

Being: \( CH_{poz} \), the lime consumed in the pozzolanic reaction; \( CH_{th} \), the initial lime content (wt. %); \( CH_{f} \), the free portlandite content; \( CH_{carb} \), the lime consumed in the carbonation reaction; \( ML_{(380-500^\circ C)} \), the mass loss between 380-500°C corresponding to portlandite dehydration; \( ML_{(500-850^\circ C)} \), the mass loss between 500-850°C corresponding to carbonates decarbonation; \( MM(CH) \) and \( MM(CO_{2}) \), the molar masses of the portlandite and \( CO_{2} \) compounds in accordance with the hypothesis considered in equation 1 and 3.

Figure 6 illustrates the comparison between the lime consumed in the pozzolanic reaction versus the lime consumed in the carbonation reaction at 28 days and 90 days of curing, respectively.
From Figure 6 it can be stated that, with exception of L3MK50, in general, the pozzolanic reaction is dominant at 28 days of curing for all mortars. In contrast, at 90 days of curing the pozzolanic reaction dominance only occurs for L1MK mortars. 

As for carbonation reaction, it is shown that, with the exception of L1MK50 and L3MK50, it increases with curing time, i.e., from 28 days to 90 days for all mortars. 

Also, if considering the pozzolanic reaction it is evident that there is a higher rate regarding L1. In the same way, considering the carbonation reaction, a higher rate is observed for compositions L2 and L3.

4. Discussion

4.1 Materials characteristics

The XRD results demonstrated that, besides calcite, the main hydrated phases present in lime-MK blended mortars are stratlingite, calcium aluminate hydrate, monocarboaluminate and portlandite. Stratlingite was favoured by mortars possessing high MK content and with increasing ageing, independently of the chosen binder:aggregate mortar ratio, and therefore more abundant with the 1:1 binder:aggregate mortar ratio.
Silva and Glasser [29] showed that stratlingite is not stable in the presence of portlandite, and Locher [31] stated that, when both hydrated phases are present, the formation of hydrogarnet occurs. The results of this research confirm these statements as can be seen in Fig. 3, for the mortars with 30% MK content at 28 days, where katoite (a low silica hydrogarnet) is shown both in the presence of stratlingite and portlandite. Since portlandite shows a remarkable decrease at 90 days, no katoite formation was detected at this age.

A problem regarding both calcium aluminate hydrate and monocarboaluminate arises, since both aluminate hydrated phases are unstable with increase of MK and curing time. As described by Silva and Glasser [29] the reason behind this behaviour is the reduction of the concentrations of Ca\(^{2+}\) and OH\(^-\) ions in the pore solution at longer curing ages.

TG-DTA results showed that, with the humid curing conditions used, the pozzolanic reaction is favoured in relation to the carbonation reaction at early ages of curing (28 days), reverting its dominance to the carbonation reaction at longer curing times (90 days) for almost all mortar compositions (except L1MK30 and L1MK50). Also, according to the results obtained, mortar L1MK50 (with 1:1 binder:aggregate ratio and 50 MK wt. %) shows the highest pozzolanic reaction, relatively to L2MK and L3MK mortars.

According to results of mechanical test, when comparing flexural and compressive strength for all mortars at all ages, some mortars evidenced mechanical resistance decrease with ageing, what can be explained by the disappearance of both aluminate hydrated phases, probably together with microcracking due to shrinkage, and also due to the increase of the water/binder ratio.

As already described previously, stratlingite is responsible for the improvement of the mechanical strength of lime-MK mortars, which increases with ageing and MK content. However, this behaviour does not correlate with the obtained mechanical results when speaking of MK30 mortars. In fact it may mean that other compounds can have a part
to play regarding the mechanical resistance of lime-MK mortars, namely calcite, calcium aluminate hydrates and monocarboaluminate, as well as calcium silicate hydrate (CSH). It is viewed that the CSH overlaps with calcite peak, as shown in Figure 3.

As for 50MK mortars, there is an increase in stratlingite content, which signifies increase of the pozzolanic reaction due to higher MK content; the mechanical results are in accordance.

### 4.2 Application to conservation purposes

The mortars used for conservation purposes should be selected taking into account practical considerations and compatibility criteria.

Mortars formulations with too high binder content, as the cases of L1 and L1MK mortars, are not frequently used for rendering, plastering and repointing applications, due to difficult workability (noticed at the experimental campaign), high shrinkage and cracking [32].

The existence of extensive pozzolanic reactions does not imply that mortars are more adequate for use in conservation of old masonry, because they might be too stiff for that purpose and turn out to be incompatible [32, 33].

Comparing the mechanical results of the analysed mortars with general values defined for compatibility with old masonry (0.2 to 0.8 MPa for flexural strength and 0.4 to 3.0 for compressive strength) [33] it can be concluded that L2MK30 and L3MK mortars are considered adequate proportions for air lime-based mortars to be applied for restoration purposes.

### 5. Conclusions

The lime-MK blended mortars described in this study presented mineralogical and mechanical strength results with interesting conclusions regarding adequate mortar formulations to be applied for the restoration of historic masonries.
The partial substitution of air lime by MK turned the hardening of air lime based mortars possible and faster even in an environment with high relative humidity and feeble contact with CO$_2$, contributing to the increase of mechanical strength of mortars at young ages. These types of mortars can be applied in situations where pure air lime mortars are not adjustable to *in situ* schedules.

The binder:aggregate ratio of mortars can lead to different levels of mechanical strength, turning the mortars adequate to be applied on different types of masonries, and the percentages of MK versus air lime are important to the balance between carbonation and pozzolanic reactions.

Mortars with low binder:aggregate ratio (1:3) seem to develop quicker carbonation, therefore consuming portlandite and hindering the development of pozzolanic reactions at short term. These mortars seem to achieve their highest strength relatively early, mainly by carbonation, between 28 and 90 days. On the other hand, mortars with higher binder:aggregate ratio (1:1) present slower carbonation rates, thus some proportion of lime is free for pozzolanic reaction during a longer period, and some increase of strength is possible at longer term, especially for high MK content.

However, mortars with high binder amounts, despite extensive pozzolanic reaction, are not adequate for use in conservation actions due to high shrinkage and incompatibility due to excessively high mechanical characteristics.

The reduction in the mechanical resistance of some compositions from 28 to 90 days is related to the calcium aluminate hydrate instability in the presence of free lime. However this instability is expected to disappear after the total consumption of free lime, either by pozzolanic or carbonation reaction.

This work is still on-going, and at 90 days of curing it is evident that there is a clear influence of binder:aggregate ratio on the mechanical and mineralogical behaviour of lime-MK mortars. The exploitation of data at higher curing ages can confirm the presently drawn hypothesis.
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