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# Modelling of slaked lime–metakaolin mortar engineering characteristics in terms of process variables

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**Abstract**

The purpose of the present study is to determine the effect of factors such as dosage, curing conditions and use of a superplasticiser admixture on the porosity, mechanical strength and composition of slaked lime (SL)–metakaolin (MK) mortars. Statistical correlations have been established to describe the mechanical properties as well as porosity and composition of the slaked lime–metakaolin mortars.

The SL/MK ratio has a moderate effect on mortar flexural and compressive strengths. The SL + MK/sand ratio is the factor with the highest impact on all the properties studied: strength, porosity and mortar composition. As this ratio increases, strength, porosity and amount of hydration and carbonation products formed in the samples also rise. The next factor by order of importance is the presence of a superplasticiser admixture, which affects porosity, strength and the amount of calcite in the sample. The presence of this superplasticiser admixture increases strength, raises the percentage of calcite in the mortars and reduces porosity. It is particularly striking that neither curing nor open air carbonation time (in the range studied) has a significant effect on the composition or porosity of the SL–MK mortars studied, although they do have a moderate effect on mechanical strength.


*Keywords:* Lime; Metakaolin; Mortars; Superplasticiser; Statistical analysis

## 1. Introduction

The protection of a weaker substratum of floors, walls or columns with slaked lime (SL) mortars and the use of these substances as bedding and pointing mortars date from early antiquity. Mortars are both highly permeable and compatible with limestone and other natural construction materials and have a low modulus of elasticity. At the same time, they are very porous and their mechanical strength and durability are low (low frost-thaw resistance, etc.).

One way to improve the strength and durability of SL mortars is to partially replace SL by other materials, such as pozzolan, clay, etc. One of the promising pozzolanic materials in this regard is metakaolin (MK), obtained by dehydrating kaolin at temperatures of from 600 to 700 °C.

MK is an amorphous material, with a very large specific surface and high acidic oxide ($Al_2O_3 + SiO_2 > 90\%$) content, which explains why it reacts so quickly and combines with such considerable amounts of portlandite. Frías and Cabrera [1,2] studied the hydration mechanism in slaked lime and metakaolin mixes reporting that lime is consumed at a very rapid rate in the initial reaction period (up to 50 h) and that the reaction mechanisms are consistent with diffusion control for the first 120 h; these authors also reported that a CSH gel was formed within 2 days, and aluminate phases 9 days after hydration.

Two competing reactions are involved in SL–MK mortars: on the one hand MK react with calcium hydroxide, leading to CSH[1] gel and several calcium silicate and aluminate hydrates ($C_2ASH_8$, $C_4AH_{13}$, etc.) [3], while on the

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[1] The following abbreviations are used in cement chemistry $H = H_2O$; $C = CO_2$; $S = SiO_2$; $A = Al_2O_3$.

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other portlandite reacts with atmospheric $CO_2$, causing carbonation of the mortar.

Both carbonation and pozzolanic reaction rates depend on environmental conditions (temperature and relative humidity (RH)): high temperature and saturated relative humidity favour pozzolanic reaction [4], while relative humidity values of around 60% favour carbonation [5]. The microstructure that develops, the composition and consequently the properties of SL–MK mortars depend on which of the two reactions prevails.

Material durability is directly related to porosity, and essentially to the distribution of pore size. Fortes-Revilla et al. [6] proved that the addition of MK to SL mortars in a proportion of 1:1 reduced total mortar porosity and induced a refinement in pore size, in particular in pores with diameters larger than 1 μm.

Little is known, however, about the effect of admixtures on SL or SL–MK mortars. Blanco-Varela and Fortes-Revilla [7] showed that chemical admixtures (plasticizers) modified the mechanical behaviour of SL–MK mortars as well as their porosity and microstructure. In general they reduced the mixing water required, while increasing its mechanical strength and diminishing porosity.

No studies have been conducted to relate dosage factors and curing conditions to the mechanical and microstructural properties and composition of SL–MK repair mortars.

The purpose of the present study is to determine the influence of a number of process variables – dosage, curing conditions and the use of a superplasticiser admixture – on the porosity, mechanical strength and composition of SL–MK mortars.

## 2. Experimental procedure

### 2.1. Materials

Table 1 shows the chemical analysis of slaked lime, sand and metakaolin used as prime materials in the mortars. Metakaolin (MK) was obtained by burning a very pure kaolin at 750 °C for 24 h. Loss on ignition at 500 and 1000 °C was likewise determined for slaked lime [8].

Eight different types of mortars were prepared with varying proportions of SL, metakaolin and sand and with or without admixtures. Mortar proportioning and dosage are shown in Table 2. The SL + MK/sand ratios used were defined on the basis of data in the literature on SL mortar dosage [9–11]. The amount of water added in the mixing process (see Table 2) was pre-determined by flow table testing to the respective Spanish standard [12]. For convenience, each mortar is assigned a serial number in which the first two numerals designate the mortar type by dosage and inclusion or otherwise of the superplasticiser admixture (Table 2), the third denotes curing time and the fourth natural carbonation time (Tables 3 and 4). The absence of a fourth numeral denotes that the sample was tested before starting the second stage of curing.

Table 2
Mortar dosage

| Mortar | SL/MK | SL + MK/sand | Admixture | Water/SL + MK |
|---|---|---|---|---|
| I.1 | 1:1 | 1:2 | Yes | 0.553 |
| I.2 | | 1:5 | | 0.768 |
| II.1 | 1:2 | 1:2 | | 0.509 |
| II.2 | | 1:5 | | 0.80 |
| III.1 | 1:1 | 1:2 | No | 0.975 |
| III.2 | | 1:5 | | 1.280 |
| IV.1 | 1:2 | 1:2 | | 1.000 |
| IV.2 | | 1:5 | | 1.330 |

Curing conditions were carefully chosen to follow the evolution of the pozzolanic and carbonation reactions versus time, and the impact of curing conditions on mortar properties. The curing temperature was held constant at 21 ± 1 °C. Mortars were initially stored in a moist closet at 100% relative humidity for 15 or 45 days, in order to keep their porous lattice water-saturated and delay $CO_2$ diffusion in specimens, reducing carbonation and favouring the pozzolanic reaction. In a second stage, samples were cured in open air at a relative humidity of 60% for 10 or 30 days, to induce the partial drying of capillary water and natural carbonation of specimens.

The admixture was a polycarboxylate polyoxyethylene (PCP). This product provides primarily for a substantial reduction in the amount of mixing water (as can be seen in Table 2) and good paste workability. The admixture was added to the mortar with the mixing water in a proportion of 2% by weight of binder [13].

### 2.2. Characterization

Powder X-ray diffraction (XRD) was employed in the mineralogical characterization of SL, sand and metakaolin;

Table 1
Chemical analysis of starting materials (wt.%)

| | IR | $SiO_2$ | $Al_2O_3$ | $Fe_2O_3$ | CaO | MgO | $SO_3$ | $Na_2O$ | $K_2O$ | $CO_2$[a] | $H_2O$[b] |
|---|---|---|---|---|---|---|---|---|---|---|---|
| SL | 0.03 | 0.39 | 0.16 | 0.24 | 72.1 | – | – | – | – | 5.52 | 20.94 |
| Sand[c] | 0.40 | 98.92 | 0.18 | 0.06 | 0.00 | 0.28 | – | – | – | – | – |
| MK[c] | 0.41 | 55.42 | 43.32 | 0.64 | 0.2 | – | – | 0.02 | 0.06 | – | – |

[a] Loss on ignition from 500 °C to 1000 °C.
[b] Loss on ignition from 105 °C to 500 °C.
[c] Digestion by alkali fusion.

Table 3
Experiment statistical design factors and levels

| Factor | Factor definition | Factor level | | | |
|---|---|---|---|---|---|
| *A* | SL/MK ratio | 1:2 | $X_A = (-1)$ | 1:1 | $X_A = (+1)$ |
| *B* | SL + MK/sand ratio | 1:5 | $X_B = (-1)$ | 1:2 | $X_B = (+1)$ |
| *C* | Admixture | No | $X_C = (-1)$ | Yes | $X_C = (+1)$ |
| *D* | Curing time | 15 d | $X_D = (-1)$ | 45 d | $X_D = (+1)$ |
| *E* | Natural carbonation time | 0 d $X_E = (-1)$ | | 10 d $X_E = (0)$ | 30 d $X_E = (+1)$ |

d = days.

Table 4
$Ca(OH)_2$, $CaCO_3$, IR, and LOI (wt.%) for mortars with admixture

| Mortar | $Ca(OH)_2$ | $CaCO_3$ | IR[a] | LOI[b] | Mortar | $Ca(OH)_2$ | $CaCO_3$ | IR | LOI |
|---|---|---|---|---|---|---|---|---|---|
| I.1.15 | 1.70 | 15.4 | 74 | 7.86 | II.1.15 | 0.33 | 10.9 | 80 | 5.81 |
| I.1.15.10 | 0.18 | 15.9 | 76 | 8.10 | II.1.15.10 | 0.34 | 10.1 | 79 | 5.33 |
| I.1.15.30 | 0.20 | 13.7 | 75 | 7.32 | II.1.15.30 | 0.30 | 12.8 | 79 | 6.66 |
| I.1.45 | 0.26 | 15.0 | 75 | 7.55 | II.1.45 | 0.17 | 9.7 | 80 | 5.28 |
| I.1.45.10 | 0.39 | 15.4 | 75 | 7.87 | II.1.45.10 | 0.09 | 12.0 | 82 | 6.23 |
| I.1.45.30 | 0.28 | 16.2 | 72 | 8.50 | II.1.45.30 | 0.13 | 8.7 | 76 | 4.92 |
| I.2.15 | 0.11 | 6.4 | 89 | 3.57 | II.2.15 | 0.18 | 5.8 | 87 | 3.17 |
| I.2.15.10 | 0.18 | 6.7 | 87 | 3.70 | II.2.15.10 | 0.45 | 5.1 | 90 | 2.75 |
| I.2.15.30 | 0.12 | 7.1 | 88 | 4.30 | II.2.15.30 | 0.37 | 5.8 | 90 | 3.04 |
| I.2.45 | 0.34 | 6.2 | 89 | 3.27 | II.2.45 | 0.14 | 4.7 | 90 | 2.65 |
| I.2.45.10 | 0.67 | 6.6 | 89 | 3.30 | II.2.45.10 | 0.10 | 4.6 | 91 | 2.50 |
| I.2.45.30 | 0.13 | 7.0 | 90 | 3.67 | II.2.45.30 | 0.12 | 5.6 | 89 | 2.89 |

[a] Insoluble residue in HCl.
[b] Loss of ignition at 1000 °C.

the diffractograms were recorded in a range of $2\theta = 5$–60° on a Philips PW-1730 diffractometer. Metakaolin was analysed using FTIR techniques on an ATI Mattson Genesis double-beam spectrometer fitted with a standard $LiTaO_3$ detector covering wavelengths ranging from 400 to 4000 $cm^{-1}$.

Mortar prisms measuring $10 \times 10 \times 60$ mm and $10 \times 10 \times 5$ mm were prepared and cured under the conditions described above. The $10 \times 10 \times 60$ mm, prisms were used to measure mortar flexural and compressive strengths at the different curing and natural carbonation ages [14]. The porosity and pore size distribution of mortars were found by analysing the $10 \times 10 \times 5$ mm specimens, previously dried at vacuum until constant weight, with a mercury Micromeritics (Autopore II 9220) porosimeter which achieved a pressure of 414 MPa.

The mineralogical composition of mortars was determined by XRD; in addition, since the main product of the pozzolanic reaction is an amorphous phase (CSH gel), the following complementary analyses were conducted:

(1) The free $Ca(OH)_2$ in the mortars was determined at the curing and carbonation ages stipulated with the ethylene glycol method [15].
(2) The calcium carbonate content in the mortars was computed from the $CO_2$ content deduced from the difference in loss on ignition at 500 °C and 1000 °C.
(3) Finally, the insoluble mortar residue in dilute HCl (IR) was also quantified using the analytical procedure described in Granizo et al. [16], which dissolves portlandite, calcium carbonate and the pozzolanic reaction products, but not unreacted metakaolin or sand (quartz).

### 2.3. Statistical analysis

The impact of a series of factors (SL/MK ratio, SL + MK/sand ratio, use of admixture, curing and natural carbonation times) on the composition, porosity and flexural and compressive strength of mortars was studied by using a full factorial experimental design ($2^4 \times 3$) to define the trials to be run.

Table 3 lists the factors addressed in the design and the levels assigned to each. Two levels were assigned to factors *A*, *B*, *C* and *D*: a "+" indicates the higher and a "−" the lower level. Three levels were defined for factor *E*, where a "−" means mortars without natural carbonation, a "0" 10 days of natural carbonation, and a "+" 30 days of natural carbonation. The response variables considered for that experiment were flexural and compressive strength, porosity and mortar composition.

STARGRAPHICS Plus software (version 3.1) was used to analyze the variance and determine the mathematical equation defining the model for the factorial experimental design [17,18]. The mathematical model used is described by Eq. (1) [19,20]:

$$R = \theta + A_1X_A + B_1X_B + C_1X_C + D_1X_D + \delta_{NE} + \delta_{AB} + \delta_{AC} + \delta_{AD} + \delta_{AE} + \delta_{BC} + \delta_{BD} + \delta_{BE} + \delta_{CD} + \delta_{CE} + \delta_{DE} + \varepsilon \quad (1)$$

where $\theta$ is the overall mean of the estimated value; $A_1$, $B_1$, $C_1$ and $D_1$ are the coefficients associated with factors $A$, $B$, $C$ and $D$, determined by least squares; $X_A$, $X_B$, $X_C$ and $X_D$ are the variables whose values are $-$ or $+$, depending on whether the levels of factors $A$, $B$, $C$ and $D$, respectively, are $-1$ or $+1$. In two-level factorial designs (factors $A$, $B$, $C$ and $D$, see Table 3), there is only one parameter per factor: the effect of each factor is defined as the expected increment in the response when the factor moves from $-$ to $+$. $\delta_{NE}$ represents factor $E$, for which three levels are defined and which assumes a different value at each level. $\delta_{AB}$ to $\delta_{DE}$ are the binary interactions, which also assume different values for each level. $\varepsilon$, representing random measurement errors, was considered to be negligible for interactions involving more than two factors.

## 3. Results

### 3.1. Mineralogical composition

Mineralogical characterisation of MK (X-ray diffraction, FTIR, $^{29}$Si and $^{27}$Al MAS NMR) has been published in previous papers [21,22]. According to the respective XRD analyses, portlandite is the majority constituent of SL, which also contains a small proportion of $CaCO_3$ ($\cong$11% by weight). Quartz is the only crystalline constituent of the sand.

The XRD findings for the mortars show that in nearly all samples the only majority crystalline compounds are quartz and calcite and the intensity of the reflections attributed to $Ca(OH)_2$ is weak, even in the samples not subjected to carbonation. The amount of calcite increases slightly when the samples are subjected to natural carbonation during the second stage of curing.

### 3.2. Mechanical strength and porosity

Figs. 1 and 2 show flexural and compressive strength for the various types of mortar studied.

Porosity of the different specimens is shown in Fig. 3. Pore size distribution studies indeed that it varies greatly in mortars with different SL + MK/sand ratios. In admixture-containing mortars (I and II), the use of a greater proportion of sand, all other factors being equal, causes a substantial rise in the volume of pores with a diameter greater than 1 μm and a decline in the volume of pores whose diameter lies between 1 μm and 0.01 μm; the most prominent effect observed in the mortars without admixture (III and IV) however, is a lower volume of pores with a diameter in the range of 1–0.1 μm.

### 3.3. Chemical composition

Tables 4 and 5 show the $Ca(OH)_2$ and $CaCO_3$ contents, acid-insoluble residue (IR) and loss on ignition at 1000 °C (LOI) for the mortars studied. The free $Ca(OH)_2$ content is very low, under 1%, in all the mortars except I.1.15.

The $CaCO_3$ content is lower in mortars with a high sand content. Mortars with greater amounts of metakaolin with respect to the amount of SL also have smaller amounts of $CaCO_3$. Calcium carbonate content is somewhat higher in mortars with the polycarboxylate admixture than in mortars with the same dosage but without the admixture.

The insoluble residue in dilute HCl acid (IR) provides a measure of the amount of sand plus the amount of unreacted metakaolin in the mortars. As Tables 4 and 5 show, the values are practically the same for mortars I.1 and III.1; I.2 and III.2; II.1 and IV.1; and II.2 and IV.2. This is because these same pairs of mortars have the same

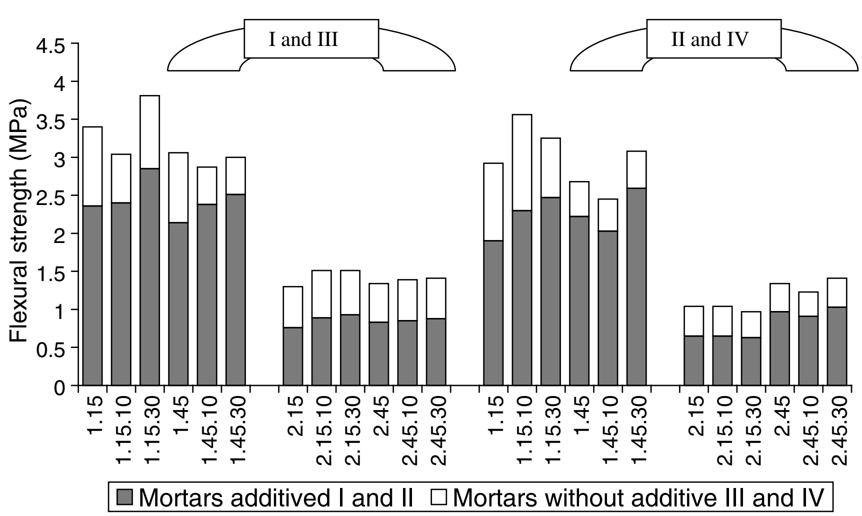


Fig. 1. Flexural strength of specimens elaborated with different type of mortar.

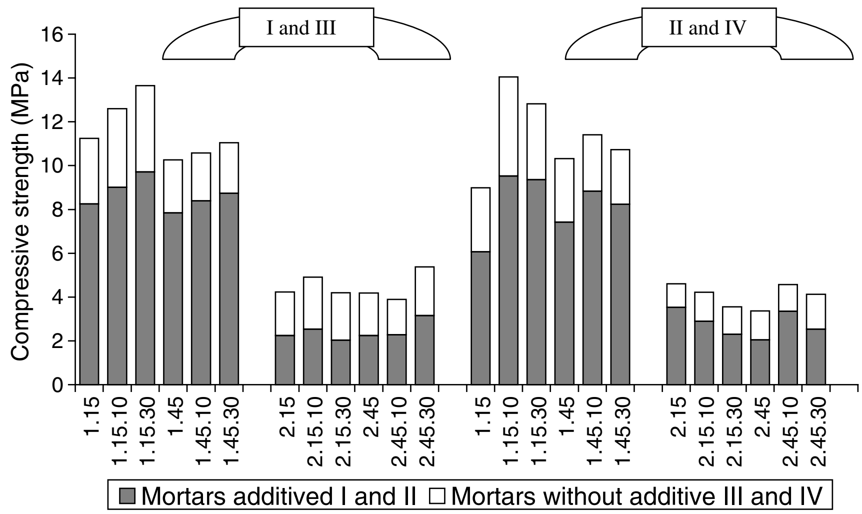


Fig. 2. Compressive strength of specimens elaborated with different type of mortar.

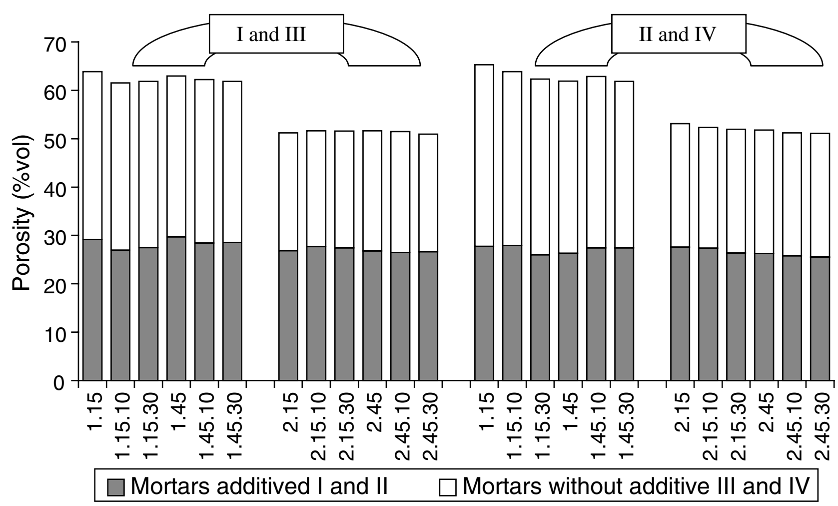


Fig. 3. Total porosity of specimens elaborated with different type of mortar.

Table 5
$Ca(OH)_2$, $CaCO_3$, IR and LOI (wt.%) for mortars without admixture

| Mortar | $Ca(OH)_2$ | $CaCO_3$ | IR | LOI | Mortar | $Ca(OH)_2$ | $CaCO_3$ | IR | LOI |
|---|---|---|---|---|---|---|---|---|---|
| III.1.15 | 0.72 | 13.1 | 74 | 7.01 | IV.1.15 | 0.58 | 9.0 | 77 | 5.43 |
| III.1.15.10 | 0.71 | 14.2 | 76 | 7.49 | IV.1.15.10 | 0.67 | 8.9 | 77 | 5.34 |
| III.1.15.30 | 0.63 | 14.6 | 75 | 7.86 | IV.1.15.30 | 0.20 | 7.6 | 79 | 4.75 |
| III.1.45 | 0.12 | 15.0 | 74 | 8.01 | IV.1.45 | 0.15 | 9.4 | 79 | 5.21 |
| III.1.45.10 | 0.94 | 13.8 | 78 | 6.98 | IV.1.45.10 | 0.12 | 9.7 | 78 | 5.47 |
| III.1.45.30 | 0.68 | 15.7 | 75 | 7.87 | IV.1.45.30 | 0.11 | 8.6 | 81 | 5.05 |
| III.2.15 | 0.23 | 6.4 | 88 | 3.48 | IV.2.15 | 0.25 | 3.8 | 89 | 2.26 |
| III.2.15.10 | 0.68 | 7.5 | 85 | 4.04 | IV.2.15.10 | 0.25 | 4.0 | 89 | 2.36 |
| III.2.15.30 | 0.43 | 6.8 | 87 | 3.75 | IV.2.15.30 | 0.28 | 5.0 | 88 | 3.03 |
| III.2.45 | 0.24 | 7.2 | 87 | 3.90 | IV.2.45 | 0.08 | 3.8 | 91 | 2.21 |
| III.2.45.10 | 0.27 | 6.0 | 87 | 3.37 | IV.2.45.10 | 0.11 | 4.7 | 89 | 2.69 |
| III.2.45.30 | 0.21 | 6.7 | 88 | 3.68 | IV.2.45.30 | 0.06 | 4.7 | 89 | 2.71 |

proportions of SL, metakaolin and sand and only differ with respect to the inclusion or otherwise of the admixture.

In the mortars studied, the portlandite reacts with the metakaolin and atmospheric $CO_2$, prompting both

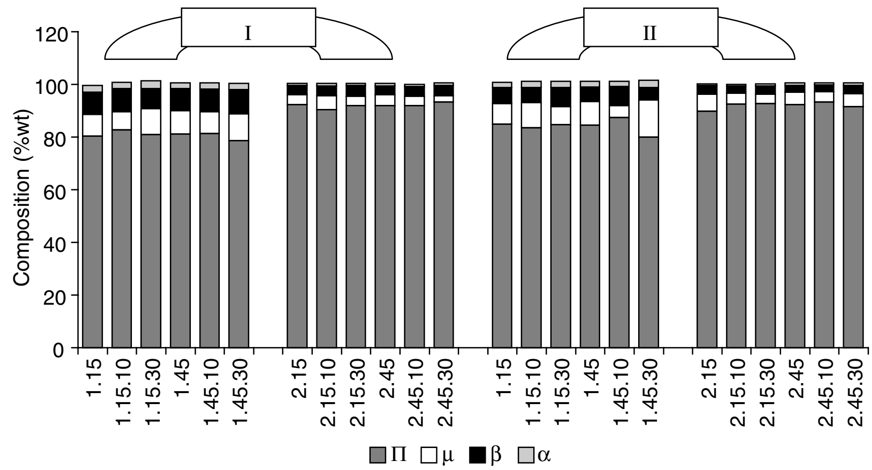


Fig. 4. Samples I and II. Values of α (CaO as portlandite), β ($CaCO_3$), μ (products formed in the lime–metakaolin reaction), and π (sand plus unreacted metakaolin) (% by wt) all of the data are referred to the samples after calcinations at 1000 °C.

pozzolanic and carbonation reactions. Fig. 4 gives the percentage of CaO present in the form of portlandite (α) or $CaCO_3$ (β), the percentage of products formed in the portlandite–metakaolin reaction (μ) and the amount of sand plus unreacted metakaolin (π); all of the data refer to the samples after calcination at 1000 °C.

The amount of pozzolanic reaction products (μ) appears to be somewhat smaller in the mortars with admixture.

The amount of sand and unreacted MK (π) is very high, over 79% in all cases, with the highest values being observed, naturally, for the mortars with larger doses of sand and MK; the use of admixture does not appear to affect this parameter (Fig. 5).

### 3.4. Statistical results

The significance of the five factors considered was obtained for each variable studied (Table 6) by conducting analysis of variance on the experimental results given in Figs. 1–4. The results in Table 6 indicate that the five factors considered do not have the same level of statistical significance. This table also shows the $p$ values (obtained with a 95% confidence interval) for each factor and the statistically significant binary interactions. The statistical relationship that describe porosity and the mechanical behaviour of SL–MK mortars under the experimental conditions are:

$$\text{Porosity (\%Volume)} = 28.59 - 0.14X_A + 2.76X_B - 1.34X_C - 0.18X_D + \delta^p_{NE} + \delta_{AC} + \delta_{BC} + \varepsilon \quad (\varepsilon = 0.79) \tag{2}$$

$$\text{Compr. st. (MPa)} = 3.9 + 0.07X_A + 1.8X_B + 1.6X_C - 0.19X_D + \delta^c_{NE} + \delta_{BC} + \delta_{BD} + \varepsilon \quad (\varepsilon = 0.61) \tag{3}$$

$$\text{Flexur. st. (MPa)} = 1.1 + 0.054X_A + 0.45X_B + 0.49X_C - 0.04X_D + \delta^f_{NE} + \delta_{BC} + \delta_{BD} + \delta_{CD} + \delta_{CE} + \varepsilon \quad (\varepsilon = 0.17) \tag{4}$$

The primary factors as well as the binary interactions of the statistically significant factors at a 95% confidence level are included in these equations. The contributions of the statistically significant binary interactions to the overall response are listed in Table 7. The values of coefficient $\delta_{NE}$ in the model equations are shown in Table 8. These

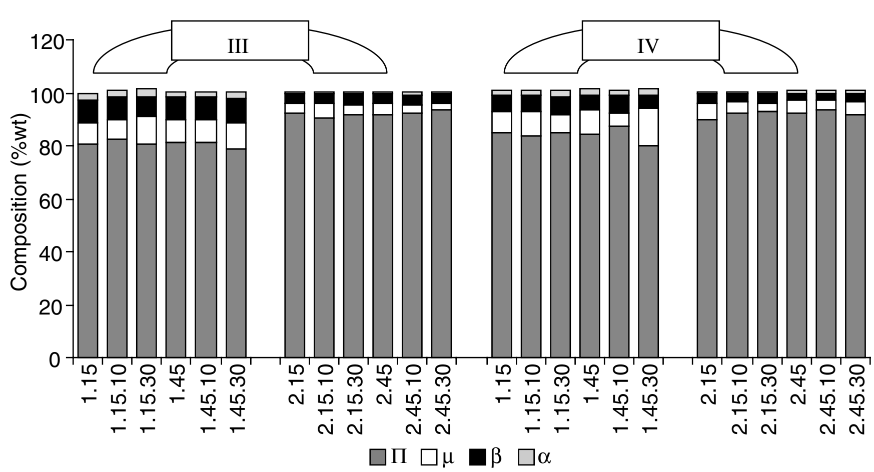


Fig. 5. Samples III and IV. Values of α (CaO as portlandite), β ($CaCO_3$), μ (products formed in the lime–metakaolin reaction), and π (sand plus unreacted metakaolin) (% by wt) all of the data are referred to the samples after calcinations at 1000 °C.

Table 6
Relevance order for the factors considered

| | Order of factors | $p$ values[a] | Binary interaction[b] |
|---|---|---|---|
| Porosity | $B^b = C^b > D > A > E$ | (0.0000 = 0.0000 < 0.6275 < 0.7114 < 0.8553) | $AC = BC = 0.0000$ |
| Compressive | $B^b = C^b > E^b > D^b > A$ | (0.0000 = 0.0000 < 0.0259 < 0.0393 < 0.4333) | $BC > BD$ (0.000 < 0.0478) |
| Flexural | $B^b = C^b > A^b > D > E$ | (0.0000 = 0.0000 < 0.0356 < 0.0921 < 0.2934) | $BC > BD > CD > CE$ (0.000 < 0.0062 < 0.0134 < 0.0269) |
| $\beta$ | $B^b = C^b > A^b > E > D$ | (0.0000 = 0.0000 < 0.0025 < 0.6312 < 0.8629) | $BC$ (=0.0000) |
| $\mu$ | $B^b > C^b > A > D > E$ | (0.0000 < 0.0135 < 0.0504 < 0.3411 < 0.6382) | |
| $\pi$ | $B^b > A^b > C > D > E$ | (0.0000 < 0.0021 < 0.0930 < 0.1845 < 0.7266) | |

[a] Confidence level 95%.
[b] Statistically significant factors.

Table 7
Values of binary interactions statistically significant between factors (in Eqs. (2)–(4))

| Porosity (2) (vol%) | | | Compressive strength (3) (MPa) | | |
|---|---|---|---|---|---|
| $X_A - X_C$; $X_B - X_C$ | $\delta_{AC}$ | $\delta_{BC}$ | $X_B - X_C$; $X_B - X_D$ | $\delta_{BC}$ | $\delta_{BD}$ |
| −1 − 1; +1 + 1 | + 0.58 | −2.24 | −1 − 1; +1 + 1 | +1.12 | −0.18 |
| −1 + 1; +1 − 1 | −0.58 | +2.24 | −1 + 1; +1 − 1 | −1.12 | +0.18 |

Flexural strength (4) (MPa)

| $X_B - X_C$; $X_B - X_D$; $X_C - X_D$ | $\delta_{BC}$ | $\delta_{BD}$ | $\delta_{CD}$ | $\delta_{CE}$ | |
|---|---|---|---|---|---|
| | | | | $X_C = -1$ | $X_C = +1$ |
| −1 − 1; +1 + 1 | +0.31 | −0.07 | +0.06 | $X_E = -1$; 0; +1 | $X_E = -1$; 0; +1 |
| −1 + 1; +1 − 1 | −0.31 | +0.07 | −0.06 | −0.09; +0.01; +0.08 | +0.09; −0.01; −0.08 |

Table 8
$\delta_{NE}$ values for the $E$ factor (time of carbonation) in Eqs. (2)–(7)

| Levels | $\delta^p_{NE}$ (Eq. (2)) | $\delta^c_{NE}$ (Eq. (3)) | $\delta^f_{NE}$ (Eq. (4)) | $\delta^\beta_{NE}$ (Eq. (5)) | $\delta^\mu_{NE}$ (Eq. (6)) | $\delta^\pi_{NE}$ (Eq. (7)) |
|---|---|---|---|---|---|---|
| −1 | −0.240 | 1.5754 | 0.558 | 0.0638 | 0.05313 | −0.0898 |
| 0 | −0.0259 | 2.0417 | −0.26 | 0.0403 | −0.29438 | 0.2421 |
| +1 | 0.270 | −3.6171 | −0.30 | −0.1041 | 0.24125 | −0.1523 |

are associated with factor $E$, time of natural carbonation. This factor adopts different values for the different levels as well as for flexural and compressive strength and porosity.

The statistical correlations describing the composition of the SL and metakaolin mortars under the experimental conditions are:

$$\beta = 5.06 + 0.11X_A + 1.84X_B + 0.26X_C + 0.014X_D + \delta^\beta_{NE} + \delta_{BC} + \varepsilon \quad (\varepsilon = 0.53) \qquad (5)$$

$$\mu = 7.07 - 0.47X_A + 2.23X_B - 0.61X_C + 0.025X_D + \delta^\mu_{NE} + \varepsilon \quad (\varepsilon = 1.61) \qquad (6)$$

$$\pi = 86.9 - 0.73X_A - 4.58X_B + 0.37X_C - 0.29X_D + \delta^\pi_{NE} + \varepsilon \quad (\varepsilon = 1.49) \qquad (7)$$

Table 9
Contribution made by the binary interaction in Eq. (5)

| $X_B - X_C$ | $\delta_{BC}$ | $X_B - X_C$ | $\delta_{BC}$ |
|---|---|---|---|
| −1 − 1; +1 + 1 | 0.43 | −1 + 1; +1 − 1 | −0.43 |

The contribution of binary interaction $BC$ described in Eq. (5) is shown in Table 9.

## 4. Discussion

Pozzolanic mortars made with slaked lime and metakaolín are promising materials for the repair of ancient masonry as pointing or repointing grout, rendering mortar, and so on. The white tone of the raw materials, the low alkali content of the mortar, improved mechanical properties and hardening times that are shorter than traditional SL mortars are some of the features that may lead to the use of these pozzolanic materials for restoration works.

Dosage, curing conditions and the use of admixtures need to be studied to develop a material with controlled and optimal properties.

The statistical analysis conducted provides information on the impact of the factors considered at the levels selected on the evolution of mechanical strength, porosity and composition in SL–MK mortars. The results obtained indicate that the statistical relevance of the five factors studied differs.

The primary factors, namely the SL + MK/sand ratio (*B*) and the presence of the admixture (*C*), together with the binary interaction *BC*, have the greatest quantitative impact on the three response variables – porosity, compressive and flexural strength – modelled in Eqs. (2)–(4). Factor *A* (SL/MK) contributes significantly as a primary factor to the flexural strength of mortars and its binary interaction with factor *C* has a statistically significant effect on the model used to describe porosity. As primary variables, factors *D* and *E*, curing and natural carbonation time, respectively, have a significant effect on compressive strength only, although their binary interactions with primary factor *C* are significant for the model representing flexural strength. Moreover, interaction BD (SL + MK/sand ratio and curing time) is significant for both the compressive and the flexural strength models.

Further to Eq. (2), when primary factor *B* adopts the value ($X_B = -1$), in other words, when the binder/sand ratio is 1:5, total porosity declines by nearly 10% (2.76) from the mean, but rises by this same amount when factor *B* adopts the value ($X_B = +1$). The use of the admixture reduces total porosity by approximately 5% (−1.34) from the mean. The interaction between factors *B* and *C* occasions modifications in porosity of about ±8%.

The effect of the admixture on porosity depends largely on the binder/sand ratio in the mortar. The admixture reduces porosity in mortars with a smaller proportion of sand ($X_B = +1$), and refines the size of the pores, prompting a drastic drop in the percentage of pores over 1 μm, whereas it increases total porosity when the amount of the sand in the mortar is five times higher than the amount of binder ($X_B = -1$); it does, however, reduce the percentage of pores larger than 10 μm in such mortars.

Finally, Eq. (2) also takes account of the statistically significant binary interaction between factors *C* (admixture) and *A* (SL/MK ratio), although this interaction has a much smaller impact on porosity than the other primary factors and the binary interaction *BC*. Mortars having admixture are less porous (0.58%) as described by binary interaction *AC* when the SL/MK ratio is 1/2 ($X_A = -1$), whereas porosity increases in the same proportion when the ratio is 1/1 ($X_A = +1$); and when there is no admixture the mortars with a SL/MK ratio of 1/1 are less porous than the ones where the ratio is 1/2.

According to these results SL–MK mortars are rather porous construction materials with a porosity that can be reduced using superplasticiser admixtures and decreasing the SL + MK/sand and SL/MK ratios.

In the mechanical behaviour models described by Eqs. (3) and (4), when primary factor *B* adopts the value ($X_B = -1$), i.e., when the binder/sand ratio is 1:5, compressive and flexural strength are observed to fall by more than 45% from the mean, while strength grows by that same percentage when primary factor *B* adopts the value (+1). The use of the admixture (primary factor $X_C = +1$) raises compressive and flexural strength by around 40% over the mean values.

There are two significant binary interactions in both models, *BC* and *BD*, although the former makes a much larger contribution than the latter. Analysing the effect of interaction *BC* it may be deduced that inclusion of the admixture enhances the flexural and compressive strength of mortars with a smaller proportion of sand and reduces strength in those with a larger proportion; in the absence of admixture the contribution of interaction *BC* to mechanical strength adopts the opposite sign. The analysis of the contribution attributed to interaction *BD*, in turn, leads to the conclusion that shorter curing times increase flexural and compressive strength in mortars with smaller proportions of sand and reduce strength in the mortars with higher proportions; similarly, at longer curing times strength in mortars with larger proportions of sand is reduced while strength is increased in mortars with smaller proportions of sand.

The model describing flexural strength (Eq. (4)) also contains primary factor *A* and two statistically significant binary interactions, *CD* and *CE*. The use of a higher SL/MK ratio raises flexural strength by approximately 5% over the mean. Finally, the conclusion to be drawn from an analysis of binary interactions *CD* and *CE* is that shorter curing and longer natural carbonation times reduce flexural strength in mortars with admixture, but raise it in those made without admixture, and vice-versa.

It must be noted here that the SL–MK mortars designed in this study do not have high mechanical strengths but their values are very much (from 2 to 5 times) higher than in traditional SL mortars [9,23]. The use of admixture and relatively high proportions of SL + MK/sand ratios increases the mean value of the compressive and flexural strength obtained in the model by 114%. Given that the pozzolanic reaction rate is slow in general, it must likewise be pointed out that due primarily to the high reactivity of metakaolin, mechanical strength is reached during the first 15 days after mixing, a finding of cardinal practical importance.

As far as composition is concerned, the portlandite content is very small in all mortars and the calcium carbonate content is high even before natural carbonation; therefore, the pozzolanic and carbonation reactions take place simultaneously and beginning with initial mixing. Consequently, the mortar binder consists of $CaCO_3$ and CSH gel.

Further to the statistical models described in Eqs. (5)–(7), factor *B* (SL + MK/sand ratio), as expected, has the greatest impact on mortar composition: the smaller the proportion of sand in the mix, the higher the binder content ($CaCO_3$ and CSH gel) and the smaller the sand + unreacted MK content ($\pi$).

Factor *C* (use of admixture) has a significant effect on the amount and type of binder in mortars (Eqs. (5) and (6)). The use of an admixture to reduce the amount of mixing water appears to favour matrix carbonation, but it significantly hampers the pozzolanic reaction. Analysing the effect of the binary interaction *BC* on the amount of calcium fixed as $CaCO_3$ ($\beta$), it may be deduced that carbonation is mainly favoured in admixture-containing mortars that also have the least amount of sand.

Finally, factor $A$ has a significant effect on the models represented by Eqs. (5) and (7). Although the values of the coefficients for factor $A$ in $\beta$ (+0.11) and $\pi$ (−0.73) are both very low, they have opposite signs, which means that smaller doses of MK yield more $CaCO_3$ and less unreacted metakaolin in mortars.

The mechanical strength values for the mortars depend on the amount of binder present, as well as porosity, and porosity is largely dependent upon the proportion of water in the mix. In mortars without admixture, increased proportions of sand lead to a very steep decline in porosity: even where the water/SL + MK ratio increases, the specific amount of water decreases by about 30% and yet strength is smaller. This may be explained by the smaller binder content in such mortars. In mortars with the admixture, porosity does not change very much with the sand dose and the decline in strength is likewise explained by the smaller proportion of cementitious phases.

## 5. Conclusions

1. The SL–MK mortars designed in this study show promise as repair mortars, pointing or repointing grouts, rendering material and so on for ancient masonry, thanks to properties such as
   (a) Their mechanical strength is very much higher than in SL mortar, but they are not strong enough to generate stress that might lead to failure in the original system to be repaired.
   (b) Mechanical strength is reached in the first 15 days after mixing.

   Moreover, commercial admixtures developed for the concrete industry also play an important role in the development of this kind of mortars, modifying their compositional, mechanical and microstructural characteristics.
2. Mortar characteristics are affected by the values assigned to the variables (dose, curing time, natural carbonation time and use of superplasticiser admixture) involved in their manufacture.Statistical relationship have been observed that describe porosity and the mechanical behaviour and composition of slaked lime–metakaolin mortars under experimental conditions, from which the following conclusions may be drawn:
   (a) The SL + MK/sand ratio is the factor with the highest impact on all the properties studied: strength, porosity and mortar composition. As this ratio increases, strength, porosity and amount of binder formed in the samples also rise.
   (b) The next factor by order of importance is the presence of a superplasticiser admixture, which affects porosity, strength and the amount of calcite in the sample. The presence of this superplasticiser admixture increases strength, raises the percentage of calcite in the mortars and reduces porosity.
   (c) The SL/MK ratio has a moderate effect on mortar flexural and compressive strength.
   (d) It is particularly striking that neither curing nor natural carbonation time (in the range considered) has a significant effect on the composition or porosity of the SL and MK mortars studied, although they do have a moderate effect on mechanical strength.

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