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Hydrophobized lime grouts prepared with microsilica and superplasticizers

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Abstract

This work reports the obtaining of lime-based grouts as repairing materials. Microsilica was added as pozzolanic additive to enhance the compressive strength of the hardened grouts. Sodium oleate, as water repellent admixture, and different superplasticizers (SPs) were also incorporated to reduce the water absorption and to enhance the injectability of the grouts. Polycarboxylate ether (PCE), polynaphthalene sulfonate (PNS), melamine sulfonate (MMS) and polyacrylic acid (PA) were tested as SPs. Regarding the fluidity of the grouts, PCE was seen to improve the injectability, followed by PNS, MMS and PA. However, PCE addition was also accompanied by a severe delay in the setting time. The other three superplasticizers did not provoke significant delays in the hardening of the samples. The water contact angle underwent an increase pointing to an effective hydrophobization of the surface as a consequence of the water repellent admixture. The combination with PCE was the most effective in keeping the water repellency in comparison with the control sample (lime grout + oleate). MMS yielded high compressive strengths and durability of the mortars, in the face of freezing-thawing cycles, was enhanced.

Keywords: Lime Superplasticizers; Microsilica; Repellent

Introduction

Filling or injection mortars, specially designed for cavity repair and masonry defects, must flow properly in a fresh state and combine strength and durability [1-5]. However, in most cases, available information is limited to the effect of a single additive, without considering the possible joint or even synergistic effect of the most interesting combinations of two or more additives and/or pozzolanic additions [6,7]. One work has been recently published raising the combination of a pozzolanic addition with some superplasticizing additives, evidencing very good and hopeful results [8]. The simultaneous combinations of two or more additives and/or additions in lime mortars have not been previously investigated by the scientific community and the study of these synergies offers very interesting possibilities of scientific-technical progress.

For the preparation of lime mortars, the bibliography has detailed the possibility of increasing resistance, shortening setting times and allowing hardening - even if the access of the CO_2 is difficult - by including pozzolanic additions to mixtures. Metakaolin has been one of the most classic pozzolans studied, but also nanosilica has been the target of some research works [9-12]. There are previous papers that study the compatibility of some of the combinations between nanosilica with polycarboxylate ethers-type superplasticizers. As a matter of fact there have been no studies of compatibility with other superplasticizers of the same type and different molecular weight or with other SPs common in the chemistry of the binders – cement mainly – such as polynaphthalene sulfonate (PNS), melamine sulfonate (MMS) and polyacrylic acid (PA). All these chemical compounds are mixing water reducers and improve workability. They present important advantages to be used in injection and filling mortars. Little is known about the activity or compatibility between these admixtures and water repellent agents, compounds that reduce the water absorption by capillarity (including oleates and stearates). The use of these water repellents is very important to minimise the water inlet to mortars, and these combinations between air lime + pozzolan + water repellent agent + superplasticizer could result in a range of mortars of enormous usefulness in the restoration of the Built Heritage, particularly for the obtaining of grouts.

Therefore, the objective of this work is to determine the behavior and compatibility in lime mortars/grouts of different combinations of additives and mineral additions, in order to optimize the mixtures and thus to obtain new mortars that could serve for the restoration of the Architectural Heritage. The following combinations will be studied: calcitic air lime with pozzolanic addition (Microsilica), superplasticizers (Polycarboxylate ether (PCE1), polynaphthalene sulfonate (PNS), melamine sulfonate (MMS) and polyacrylic acid (PA) and a Water repellent (Sodium Oleate (O)).

Materials and methods

Preparation of the mortar. Mixing proportions

The weigth proportions of the mortars were: 25% slaked calcitic lime supplied by Cal Industrial S.A. (Calinsa Navarra), classified as CL-90 by European regulations, 75% calcareous sand (Class AF-T -0/1-C sand, supplied by HORPASA Group). In addition, when necessary, the following components were added with respect to lime: 20% mineral pozzolan (Microsilica, supplied by ULMEN Europa), 0.5% water repeller (sodium oleate, provided by ADI-CENTER) and superplasticizer added in two different dosages 0.5% and 1% (PCE1, BASF's Melflux commercial product; melamine sulfonate, BASF’s Melment F10; polynaphthalene sulfonate, marketed as Conplast SP340 Fa of FOSROC International and polyacrylic acid, of Sigma-Aldrich). The mixing water was established by 31%, resulting from an adjustment of the water demand of the control mortar (additives/admixtures-free) to obtain a fluidity – as measured in the flow table test – around 185 mm.

For the preparation of the pastes, lime and the required amount of calcitic sand (limestone aggregate) were blended for 5 min using a solid-admixtures mixer BL-8-CA (Lleal, S.A., Spain). Afterwards, the necessary water and superplasticizers were then added and mixed for 90 s at low speed and adjusted according to UNE-EN 196-1 [13], in a Proeti ETI 26.0072 (Proeti, Madrid, Spain) mixer.

Mortar samples were moulded in prismatic 40 × 40 × 160 mm, stored at 20 °C and 60% RH and demoulded 7 days later. Different curing times were considered: 7, 28, 91, 182 and 365 days. In order to make the results representative, three replicates of the mortars were tested at each curing time.

Fresh-state tests

The tests of the mortars at plastic state started with the slump measurements, which were recorded after 15 strokes of the flow table, 1 per second according to the indications of the standard UNE-EN 1015-3.

Then the period of workability of the material was determined according to standard UNE-EN 1015-9 [15]. Every 15 minutes a probe was slowly introduced, scoring the weight. When this weight was higher than 1500 g, the assay was finished.

All these experiments were carried out by triplicate and the depicted values are an average value of all the recorded measurements.

Hardened-state tests

Regarding the hardened state study, prismatic specimens with dimensions of 160 x40x40 mm were prepared in Proeti C00901966 moulds. For the filling and compaction the standard UNE-EN 196-1 was carried out to perform the filling in two layers and using to compact each layer an automatic compactor (IBERTEST iB32-045E-1), eliminating the air bubbles present in the mixture. Finally, the excess of mass was eliminated with a rule. The prepared grouts were cured at 20º C and 60% RH and demoulded 7 days later.

The mechanical resistances were measured at 28, 91, 182 and 365 days, to observe possible modifications over time. For all these measurements, 3 specimens were tested, in order to obtain representative values. For the compressive strength tests, a compression breaking device Proeti ETI 26.0052 was used at a breaking speed 5-50 KP $\cdot$ s^{-1} with a time interval between 30 and 90 seconds.

In hardened specimens different characterization methods were performed. For thermal analysis, a simultaneous TG-sDTA 851 Mettler Toledo thermoanalyzer device (Schwerzenbach, Switzerland) was used under the following experimental conditions: alumina crucibles, temperature range from 25 to 1000 ºC, and a heating rate of 10 ºC·min-1 under static air atmosphere.

The porous structure of the material was studied by Mercury Intrusion Porosimetry (MIP), using a Micromeritics AutoPore IV 9500 equipment with a pressure range of 0.0015-207 MPa, which automatically recorded the pressure, pore diameter and volume of mercury intrusion.

For the durability studies, prismatic samples (prepared and cured for 28 days as described before) were tested to assess the durability. Hardened grouts were subjected to Frost resistance, which was determined by means of freezing-thawing cycles. The cycles consisted of water immersion of the samples for 24 h and subsequently freezing at -10 ºC for 24 h. For these experiments, a CARAVELL 521-102 freezer was used.

The evaluation of the hydrophobicity of the sample was carried out with a measuring instrument of the contact angle OCA 15EC Dataphysics. In this way it was possible to determine the contact angle of a drop of water deposited on the surface of the sample, and the time for the absorption of the same by the material.

Results and discussion

Mortar Properties in Fresh

Bulk density

Comparing the results, the fresh grout of plain lime (Lime in Figures) is denser than the control samples obtained by combination of Lime-Oleate (L-O) and Lime-Microsilica-Oleate (L-M-O), as shown in the Figure 1.

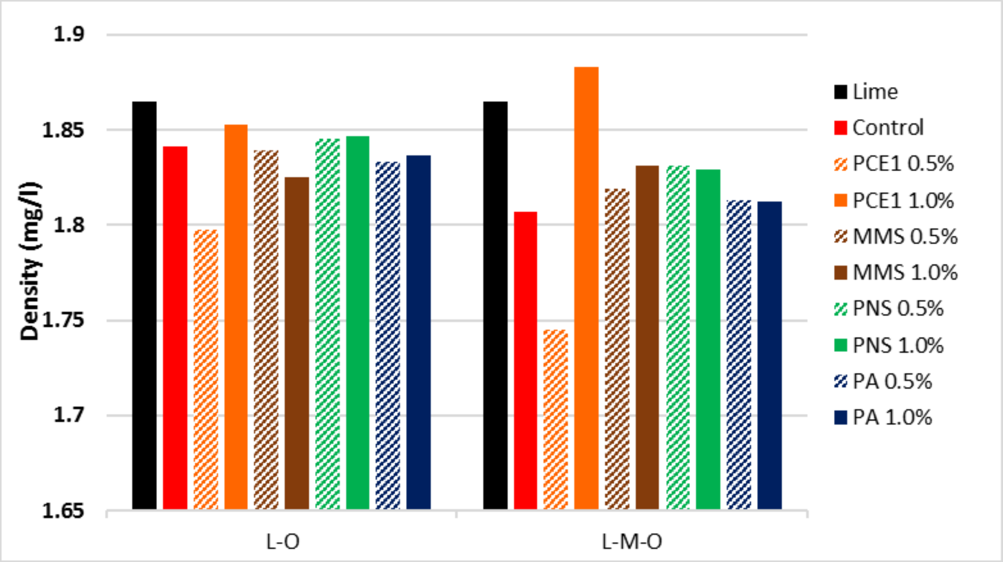


Figure 1. Density of the different mixtures

However, by adding the different superplasticizers, as shown in Figure 1, there are changes in the density of all bulks. In the case of PCE1 in the Lime-Oleate (L-O) and Lime-Microsilica-Oleate (L-M-O) mixture, the density values decreased when a dosage of 0.5% of SP was added, while increased when the SP dosage was 1%. When using PCE1 in the L-M-O mixture, the density is the lowest with the 0.5% dose and is the highest with 1% dose. When using MMS in the L-O mixture, the density decreased for 1% dose, and increased for the others. When PNS is used in each mixture with both percentages, bulk density raised. As for the PA, the density was very similar to SP-free mixtures (Control) in all the cases.

Air content

The experimental values of air content of the fresh pastes were also determined and collected in the Figure 2. Although values underwent small variations, there is a general trend showing an increase in the air content in all the samples when any of the additives was incorporated to the lime. The presence of the polymer PCE1 exerted an influence on the density and air-entrained values. PCE1 increased the air-entrained during the mixing process when was added in 0.5%, thus reducing the density (Figure 1). Conversely, the incorporation of the other superplasticizers gave rise to lower levels of air content, thus achieving comparatively denser packing systems, but in all cases the percentage of air content are greater than the pure lime. The excess in the air-entrained together with the low density of the fresh paste could involve a porosity increase after the hardening of the sample, as will be discussed below.

This performance (increasing in entrained air and a parallel density reduction) may be ascribed to the tensioactive character of the admixtures. The SPs, as well as the water repellent agents, are characterized by a dual molecule, showing a non-polar part area and also a polar segment. During the mixing process, these admixtures can be distributed at the interface area between the aqueous phase and the air, stabilizing air bubbles and giving rise to the observed values.

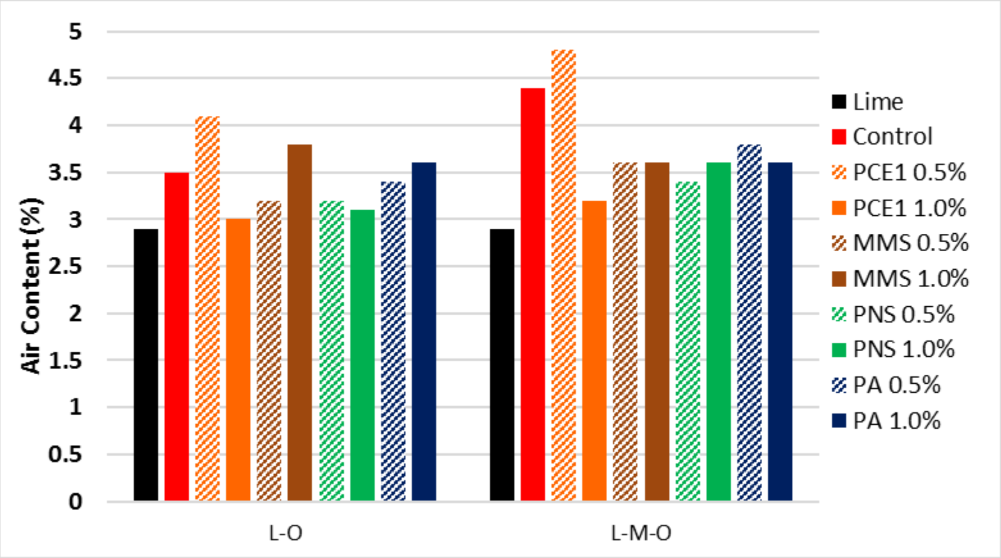


Figure 2. Air content in the different mixtures

Fluidity and workability (open time)

The fluidity was studied for the L-O and L-M-O mixtures, with and without the presence of superplasticizer. The Figure 3 shows how the fluidity of the lime grouts is affected after mixing with a water repellent agent and with a pozzolan. As it can see the L-O mixture showed a lower fluidity, while the presence of the pozzolanic addition (M) resulted in a fluidity increase. This finding can be explained as a consequence of the spherical shape of the microsilica that increases spread by allowing the lubrication of the fresh grout. The value of the L-O mix was seen to be very similar to the one of the pure lime.

Figure 3 depicts the spread values of fresh grouts with superplasticizer. The Polyacrylic Acid (PA) 1% decreases the fluidity as compared with the value of the control mix. The lowest dosage (0.5%) gave rise to a value very similar to that of the pure lime. When incorporating PNS the spread value increased in all cases with both dosages, depicting a very similar behavior to the one observed when MMS was used. After the addition of PCE1 at any dosage, the fluidity of the mixture dramatically increased, exceeding the value of 300 mm, resulting in a high-fluidity mixture. The efficiency of polycarboxylate ether derivatives has been mentioned in the literature in lime and cement systems, and is supported on the strong effect of the steric hindrance (more effective) of these additives compared with the electrostatic repulsions (less efficient).

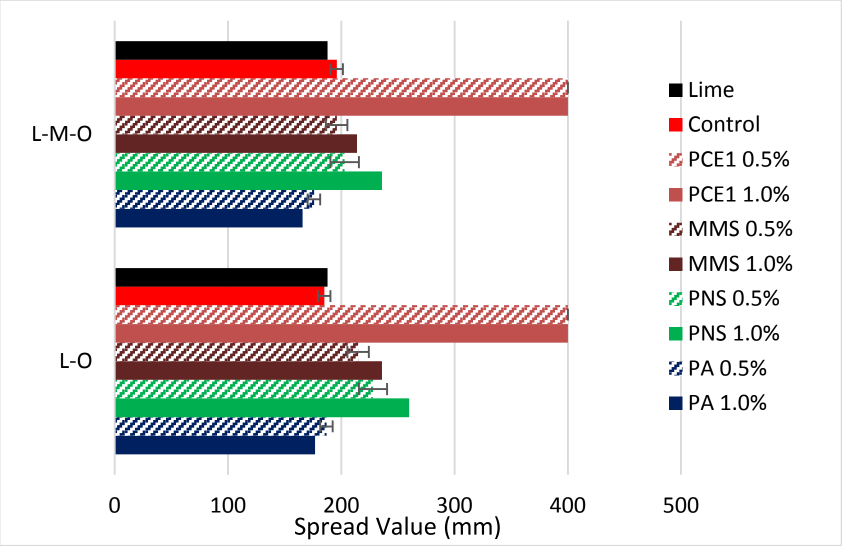


Figure 3. Fluidity of the different mixes

The workability of the different mixtures is gathered in the Figure 4. The addition of the sodium oleate accelerates the setting time of the sample, while – surprisingly- the pozzolanic agents delayed it.

The workability suffered substantial changes when the SPs were added to L-M-O grouts. The setting time whith PCE1 is so high that this grouts would not be able to be used in practical applications. For all mixtures (L-O, and L-M-O) the addition of SP (except PCE1) considerably shortened the setting time. This finding could be also helpful to achieve a workability improvement but without a delay in the setting time. In all cases the use of a 0.5% dosage was better than the use of 1% (except when PA is used).

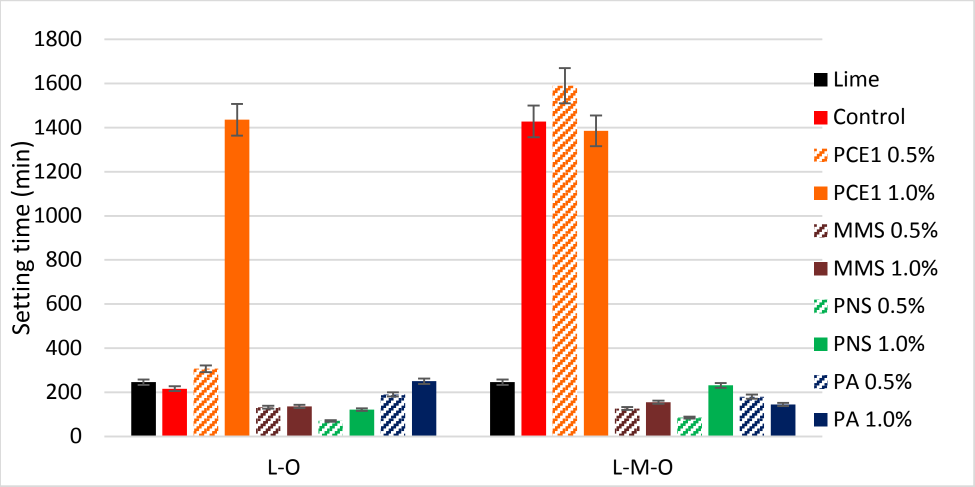


Figure 4. Workability of the different mixes

Hardened-state Properties

Compressive Strength

Carbonation has a significant influence in the hardening process along time in lime-based systems. The mechanical strengths increase over time due to the carbonation process, resulting in the formation of $CaCO_3$. Accordingly, on average, the highest values of compressive strength were obtained at long-term curing times, usually after 365 curing days (Figure 5 and 6).

For the control mix L-O at 365 curing days, without the addition of the SPs, its compressive strength was lower than that of the plain lime mortars (1.5 MPa) which could be ascribed to the interference of the sodium oleate with the lime carbonation process, as will be discussed below.

For samples with 0.5% SP at 365 curing days, samples exhibited higher compressive strength than the plain lime mortars (except in the case of PA). When a dosage 0.5% PCE1 is used in the L-O mixture, after 365 curing days, the mechanical strength was the highest (Figure 5).

When 1% SP is used, mechanical strengths increased at 365 curing days in all mixes except in the L-O mixture with PA (Figure 6). In the case of MMS strength underwent a clear increase and exhibited the highest compressive strength after 365 curing days. With respect to PA in all cases the compressive strength decreased and the use of this superplasticizer provides the lowest compressive strengths.

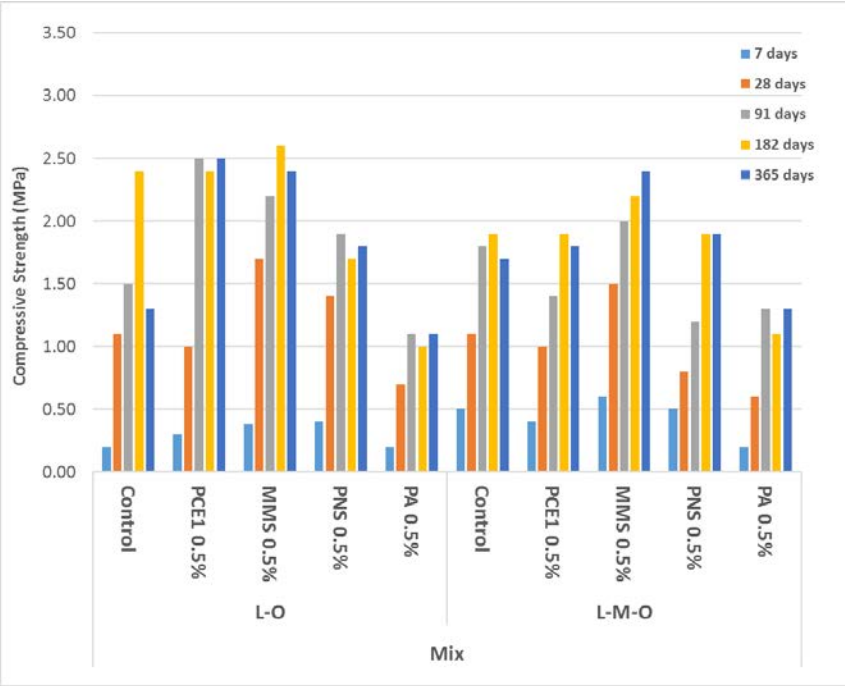


Figure 5. Compressive strength in the Hardened Mortars at different times (mixtures with 0.5% of superplasticizer)

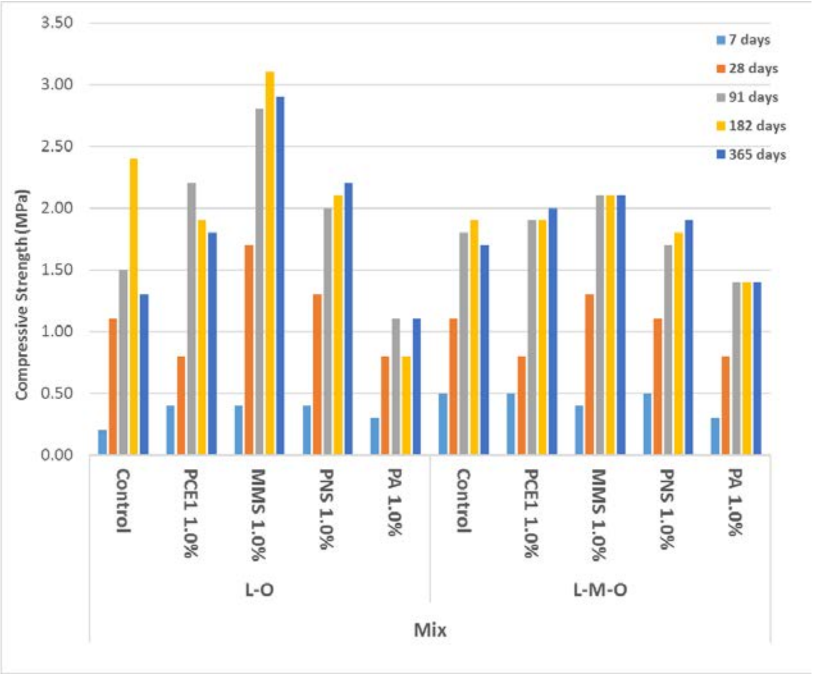
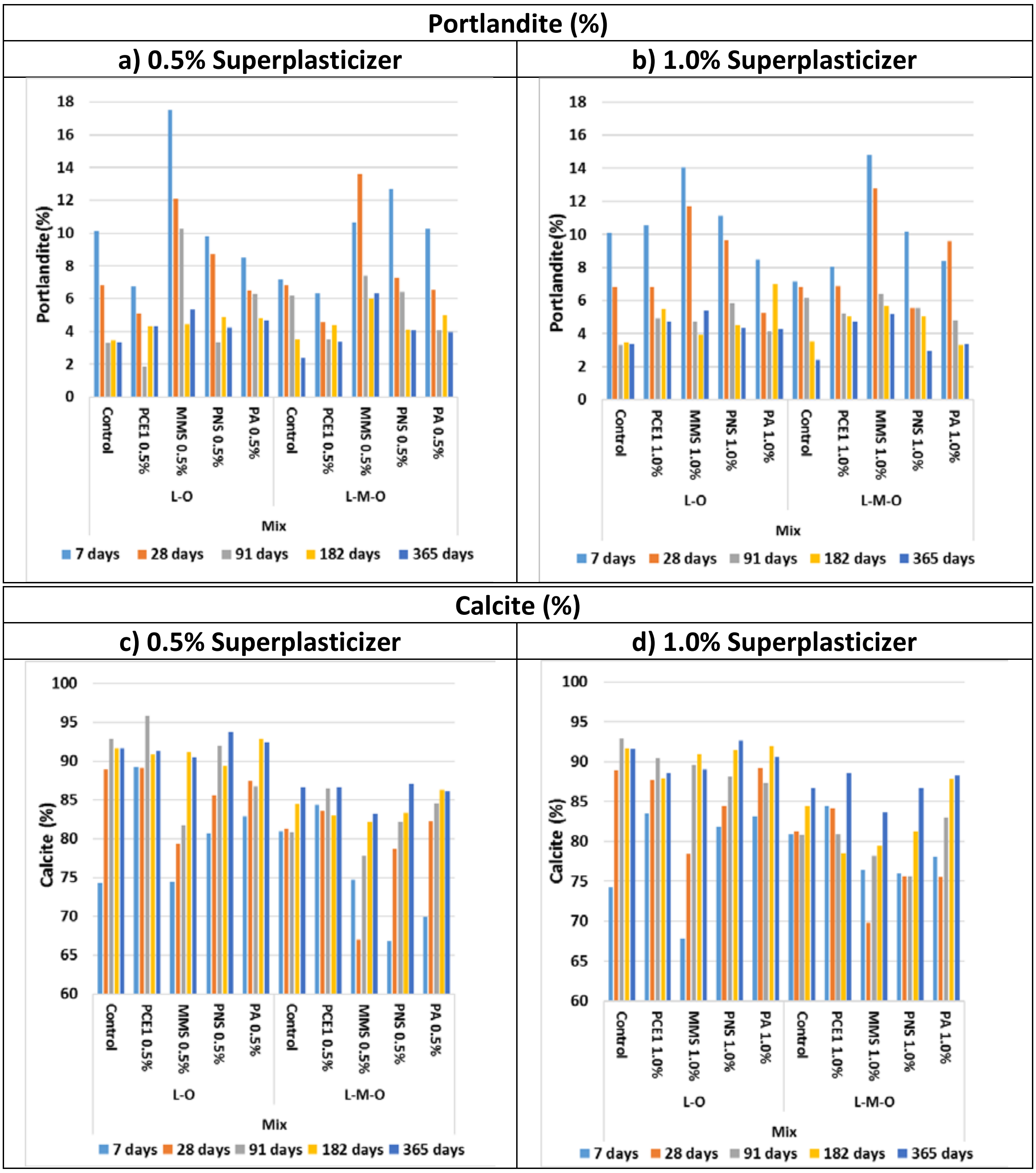


Figure 6. Compressive strengths at different times (mixtures with 1.0% of superplasticizer).

TG-DTA

The rate of carbonation and the pozzolanic reaction at the different curing times were followed by TG-DTA analyses. Previous works also correlated the structure of the materials with the TG measurements. Figures 7 depicts the percentages of $Ca(OH)_2$ and $CaCO_3$

calculated from TG weight loss due to dehydroxylation of portlandite at ca. 450ºC, and weight loss owing to the calcite decomposition at ca. 800ºC.


Portlandite (%)

a) 0.5% Superplasticizer

b) 1.0% Superplasticizer

Calcite (%)

c) 0.5% Superplasticizer

d) 1.0% Superplasticizer

Figure 7. Percentages of Portlandite (Ca $(OH)_2$) and Calcite ($CaCO_3$) of grouts at different curing times.

The degree of carbonation was helpful to understand these results: the presence of the different SPs clearly hindered the carbonation as confirmed by the thermal studies. The quantitative values obtained by TG (Figure 7) showed that the presence of any superplasticizer's doses yielded comparatively higher content in $Ca(OH)_2$. Comparing the control samples of L-O and L-M-O, a reduction in $Ca(OH)_2$ was observed due to the presence of microsilica because a pozzolanic reaction between the lime and the microsilica could be expected (Figure 7a and 7b). When PNS was used in L-O and L-M-O mixtures both at 0.5%

and 1%, the amount of calcite increased, thus suggesting that this SP did not interfere with the carbonation of the lime grout (Figure 7c and 7d).

Porosity measurements

Pore size distribution measurements (Figure 8) carried out by MIP showed that the addition of the pozzolanic additive reduced porosity about 1 µm in diameter due to: (i) the filling effect of the microsilica; and (ii) the pozzolanic reaction. In addition, the small capillary pores attributed to the formation of C-S-H increased (see the range pores between 0.1 and 0.01 µm). The reduction of larger pores explains the increase in mechanical resistances as a result of the presence of microsilica.

In the case of the L-O mixture (Figure 8A and 8B) with SP, the presence of PCE1 gave rise to a drop in the amount of pores about 1 µm, but, it permits the appearance of pores in the range of 6 to 11 microns. In the case of L-M-O mixture plus SPs (Figure 8C and 8D) the behavior was very similar without the presence of them, except in the case of the PCE1 where there is amount reduction of pores about 1 µm.

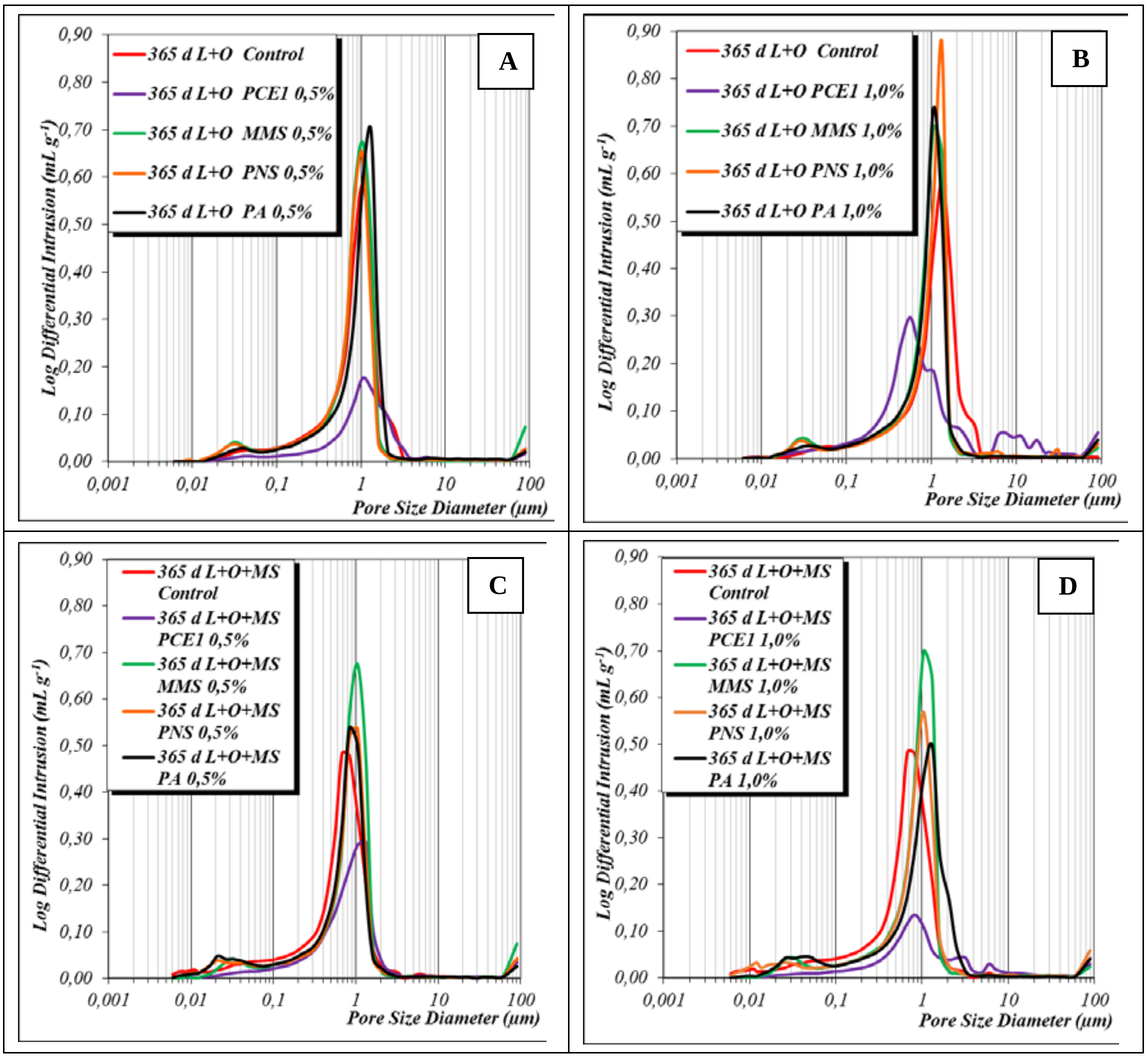


Figure 8. Pore size distributions of different samples after 365 days of curing.

Freezing-thawing

The plain grouts subjected to frost resistance test (freezing-thawing (F–T) cycles) underwent serious decay leading to the total destruction of the sample after just one cycle (Fig. 9).

Figure 9. Pure air lime grouts subjected to one freezing-thawing cycle

Fitting itself to a dosage-response pattern, the incorporation of sodium oleate clearly enhanced the F-T durability of the grouts. It can be observed (Figure 10A) that L-O control sample can endure up to 18 F–T cycles displaying serious decay only in the last cycle. However F-T endurance provided by the pozzolanic admixture included in lime mortars with the incorporation of microsilica changed this behaviour: the sample of L-M-O control showed serious decay after just two cycles (Figure 10A). This behavior could be explained as a consequence of the interaction between microsilica and sodium oleate. The SP addition involved different performance and some of grouts withstood more F-T cycles. The decrease in the mean pore size hindered the absorption of liquid water, preventing its later freezing and expansion damage, and consequently, increasing the durability of this type of grouts.

The increase in the percentage of SP did not enhance the F-T resistance of the samples. However, each one of the superplasticizer imparts a different performance. All the superplasticizers in the case of the samples of L-O, decreased the durability of the samples and in the case of the mixture of L-M-O, SPs were helpful to improve the durability. PNS yielded the worst results in terms of F-T endurance, whereas 0.5% of PCE1 enhanced the durability in the sample of L-M-O. For all the conditions, the durability of mixtures containing MMS was rather high.

Hydrophobicity

The static water contact angle (WCA) and the water absorption time (i.e., the vanishing time of the water drop after its deposition, water drop lifespan, of interest for very porous substrates) were measured for the different grouts. Samples were cured for 365 days. The results are shown in the Table 1.

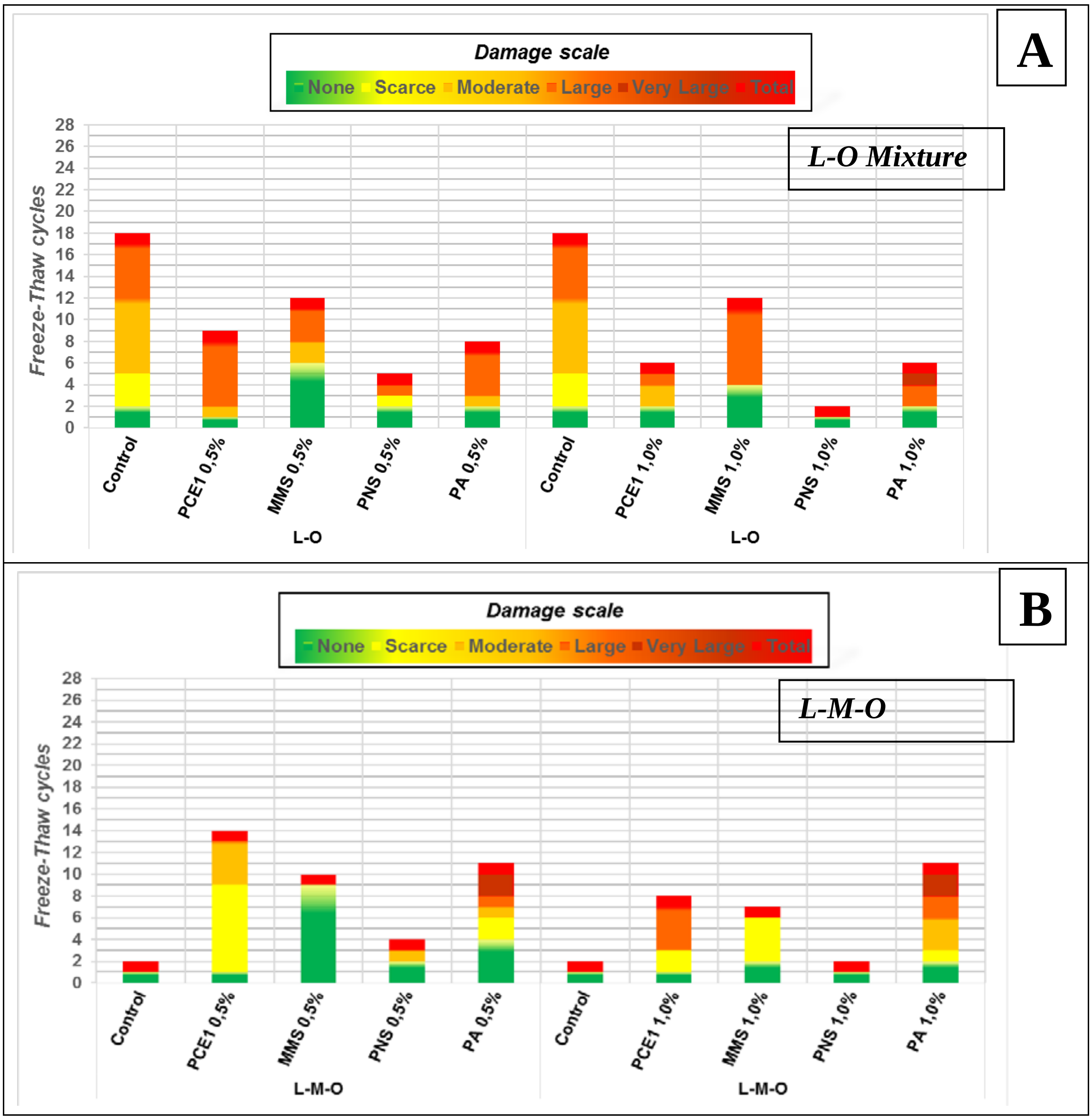


Figure 10. Alteration degrees of grouts after freeze-thaw cycles.

Table 1: Contact angle Measurement Results

Mixture	Contact angle	Full Absorption of the drop of Water and disappearance in short time interval
Lime + Oleate	75.0	No
Lime + Oleate + Microsilica	59.2	No
Lime + Oleate + PCE1 1%	66.8	No
Lime + Oleate + MMS 1%	53.5	No
Lime + Oleate + PNS 1%	29.4	Yes
Lime + Oleate + P.A. 1%	58.2	No
Lime + Oleate + Microsilica + PCE1 1%	95.1	No
Lime + Oleate + Microsilica + MMS 1%	30.2	Yes
Lime + Oleate + Microsilica + PNS 1%	29.6	Yes
Lime + Oleate + Microsilica + P.A. 1%	13.7	Yes

The mixture with the best hydrorepellency was the one with Lime + Oleate + Microsilica + PCE1 1%, due to: (i) the lowest total porosity of this grout among the all tested; (ii) PCE1 does not interfere with the oleate water-repellent activity, resulting in two highly compatible additives. The most hydrophilic mixture was the Lime + Oleate + PNS 1%, which raises the hypothesis - to be confirmed - of a chemical interaction between PNS and sodium oleate, in such a way that the water repellent action of the oleate drops, increasing the rate of water absorption. It should be noted that the hydrorepellency in all mixes was a superficial phenomenon, due to the tensioactive characteristics of sodium oleate. The hydrophobic part was exposed on the surface (air phase) during the mixing process with aqueous dispersion. However, in internal fragments of the samples, it was not possible to measure the WCA as a consequence of a dramatic reduction of the hydrophobicity (the water drop disappeared inmediately absorbed by the sample), indicating that the hydrophobization took place mainly at a superficial level.

Summary of results

In Table 2 all results are summarized, numbering and giving a grade in each test to from 1 to 4, where the number 1 refers to the sample that shows a result similar to that of a common lime grout and the number 4 represents an improvement in the tested mix. It has been considered improvement, for the injection grouts studied, and always within reasonable limits, an improvement in fluidity (workability), a shortening of the setting time (usually high for lime-based materials), an increase in the compressive strength developed, a porosity reduction and a hydrophobic surface that generates water repellency to minimise absorption and prevent deterioration and F-T endurance.

Table 2. Summary of the results of the tests carried out, both fresh and hardened to the mortars studied

Mixture	Property						
	Fluidity	Setting Time	Compressive Strength	Porosity	Freezing-thawing	Water contact Angle	Global Qualitative Rating
Lime	1	1	1	1	1	1	6
Lime + Oleate	1	3	1	1	3	4	13
Lime + Oleate + Microsilica	2	1	2	2	1	2	10
Lime + Oleate + PCE1 0.5%	4	2	4	4	2	3	19
Lime + Oleate + MMS 0.5%	2	3	4	2	2	3	16
Lime + Oleate + PNS 0.5%	2	4	3	2	2	2	15
Lime + Oleate + P.A. 0.5%	1	1	1	2	2	3	10
Lime + Oleate + PCE1 1%	4	1	2	4	2	3	16
Lime + Oleate + MMS 1%	2	3	4	2	2	3	16
Lime + Oleate + PNS 1%	3	4	3	1	1	2	14
Lime + Oleate + P.A. 1%	1	1	1	2	2	3	10
Lime + Oleate + Microsilica + PCE1 0.5%	4	1	1	3	2	4	15
Lime + Oleate + Microsilica + MMS 0.5%	2	3	3	2	2	2	14
Lime + Oleate + Microsilica + PNS 0.5%	3	4	2	1	2	2	14

Mixture	Property						
	Fluidity	Setting Time	Compressive Strength	Porosity	Freezing-thawing	Water contact Angle	Global Qualitative Rating
Lime + Oleate + Microsilica + P.A. 0.5%	2	2	1	1	2	2	10
Lime + Oleate + Microsilica + PCE1 1%	4	1	2	4	2	4	17
Lime + Oleate + Microsilica + MMS 1%	2	3	2	2	2	2	13
Lime + Oleate + Microsilica + PNS 1%	3	2	2	1	2	2	12
Lime + Oleate + Microsilica + P.A. 1%	1	3	1	1	2	2	10

As it can be seen, the mixture that showed similar value to that of the plain lime grout was Lime + Oleate + Microsilica + PA (in both percentages 0.5% and 1%), while the mixture Lime + Oleate + PCE1 0.5% is the one showing the most favorable changes in all charateristics studied, being the mixture with the greatest compressive strength, best fluidity, lowest porosity and also was the samples with the highest hydrophobicity. In addition, the workability of this mixture improves with respect to control without superplasticizer.

Conclusions

Through this study with a scientific and technical point of view was able to determine the behavior and the compatibility existing in lime-based grouts and mortars with various combinations of additives and mineral additions. This paper describes the behavior of the different mixtures between calcitic aerial lime, pozzolanic additions, superplasticizers and water-repellent agents. The results are favorable for using some of these grouts in the restoration of Architectural Heritage, resulting in the best mix of Lime + Oleate + PCE1 0.5% that improves the properties of a plain lime grout. Adjustment of the dosages of the superplasticizers should be carried out depending on the desired injectability.

Acknowledgments

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