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Department of Civil Engineering
Aristotle University of Thessaloniki

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Design of repair air lime mortars combining nanosilica and different superplasticizers

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Abstract: This contribution dealt with the design of different air lime mortars and pastes by combining a nanostructured pozzolanic additive, nanosilica, and different dispersing agents, superplasticizers (two different polycarboxylate ethers (PCE), a polynaphthalene sulfonate-based polymer (PNS) and a lignosulfonate (LS)). In pure air lime systems, the highest effectiveness was shown by the PCE1, whereas the PNS was the less effective superplasticizer. In samples with nanosilica, the PCE1 was also the most effective superplasticizer. LS was seen to be effective at low dosages. In the presence of the pozzolanic additive, there was a high consumption of polycarboxylates. Nanosilica provided no “active” adsorption sites, resulting in a slight decrease of the zeta potential values. PCE1 showed low adsorbed amounts, better dispersing action and required lower dosage of plasticizing agent. There was a positive combination between lime mortars with nanosilica and polycarboxylates, which resulted in a mechanical strength improvement. Also the combined presence of nanosilica, for example, with PNS or with LS yielded better compressive strengths, being LS more effective than PNS: SEM images showed the better formation of C-S-H phases in LS-mortars.

Introduction

To ensure a suitable fluidity of renders and grouts the use of plasticizing admixtures seems to be imperative [1,2]. Superplasticizers (SPs) are cement admixtures frequently used to reduce the water demand in order to increase the strength of material and to enhance the flowability of the fresh mortar yielding workable materials. SPs with different chemical compositions have been employed for these purposes: polycarboxylate ether derivatives (PCEs), lignosulfonates (LS), polynaphthalene sulfonate-based (PNS) polymers, etc. [3]. For air lime mortars, the use of pozzolanic additives, so-called supplementary cementing materials (SCMs) to shorten the setting times and to increase the strength is a common practice. Among them, nanosilica (NS), added as a colloidal suspension to air lime mortars, has shown very interesting performance, as a result of its filler effect and of the generation of calcium silicates hydrates (CSH) [4]. The presence of NS could affect the interaction

between the superplasticizers and the particles of the binder [5,6]. This work focuses on the behaviour of different SPs in air lime mortars modified upon the addition of pozzolanic NS.

Materials and methods

The new mortars (1:3 w/w lime:aggregate) were prepared by mixing air lime (CL90), calcitic sand and the required amounts of dry powdered admixtures (SPs) and the required volume of the colloidal nanosilica suspension. Dry components were blended for 5 min. Then mixing water (28% by weight of dry mortar) and, when required, the pozzolanic additive as a NS suspension, was incorporated and mixed for 90 s at low speed. Table 1 shows the mix proportions of the samples. The consistency of the suspensions was assessed through the mini-slump flow spread after 15 jolts. The study of the interaction between the SPs and the air lime and NS was performed by means of potential zeta's experiments in the solid/liquid interface. To this aim, suspensions with lime and 25 g of NS per 140 mL of water were prepared and allowed to react for 30 min to ensure the pozzolanic reaction to take place. SPs (1% w/v) solutions were used as titrants.

For the study of hardened state properties, mortars were moulded in prismatic 40x40x160 mm casts, stored at 20 °C and 60 % RH and demolded after 5 days. Samples were tested at different times, but only results at 7 and 91 days will be shown in this work. Samples collected from the mortars were ground and measured by powder X-ray diffraction (XRD) in a Bruker D8 Advance diffractometer, and also by FTIR-ATR and TG-DTA. Compression strength tests were done on the two fragments of each specimen resulted from previous flexural tests (rate of loading was 50 N/s). For SEM examination, a Hitachi S-4800 scanning electron microscope coupled to an EDS detector was used. Before SEM-EDS analysis, samples were coated with a gold film.

Table 1. Admixtures proportion of the studied samples of lime mortars

Sample	PCE1 (wt. %)	PCE2 (wt. %)	PNS (wt. %)	LS (wt. %)	NS (wt. %)
S1	0	0	0	0	0
S2	1	0	0	0	0
S3	1	0	0	0	20
S4	0	1	0	0	0
S5	0	1	0	0	20
S6	0	0	1	0	0
S7	0	0	1	0	20
S8	0	0	0	1	0
S9	0	0	0	1	20

Results and discussion

Studies on the fresh state of the mortars

Fig. 1 shows the flowability results of the samples. It can be seen that in plain air lime mixtures, the addition of the assayed SPs increased the fluidity. The value of flowability in the control group (S1, admixture-free sample), with only lime and aggregate, is 173 mm. Therefore, it can be concluded that the presence of SPs, acting as water reducing agents, gave rise to an increase of the fluidity of the air lime fresh samples. Similar results were described for cement-based matrices [7]. The first polycarboxylate derivative, PCE1, turned to be the most effective in increasing the fluidity of the pastes: in plain air lime samples, slump values were beyond the limits of the mini slump-flow test (> 300 mm). PNS-based polymer also increased largely the fluidity. The slump values from sample underwent an increase of ca. 45 %.

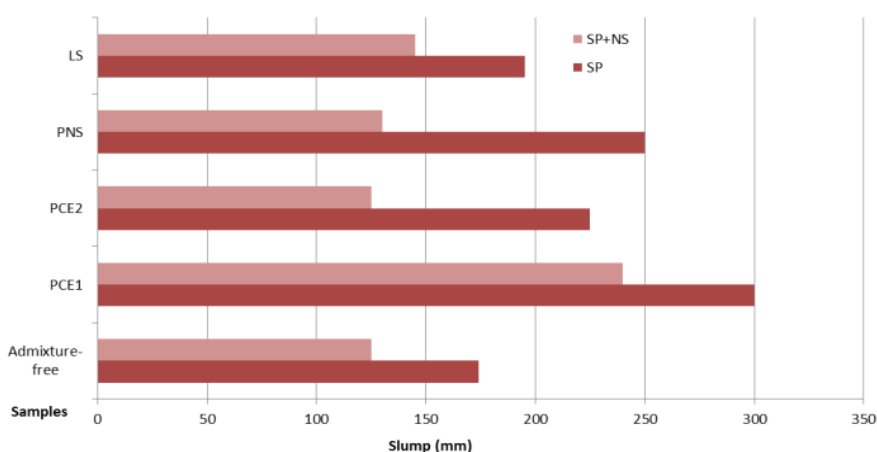


Fig. 1 Slump values corresponding to the different admixtures

In the same Fig. 1 it can be seen that the addition of NS caused a clear reduction in the values of fluidity in all the samples studied. The small particle size of NS could account for this fact, since low size particles increase the water demand to achieve a similar consistency [8].

The slump retention over time of the pastes containing SPs (0.5 wt. %) and/or pozzolanic additive (20 wt.% of NS) was assessed by measuring the slump loss over time in minutes (Fig. 2 and Fig. 3). In all instances, results showed that PCE1 induced the largest dispersing ability over time. The slump values also allowed observing that NS-bearing pastes presented low fluidity, reaching only values of slump between 115 and 142 mm (Fig. 3). The differences found in the performance of the different SPs could be explained taking into account the different molecular architecture and anionic charge densities of the

polymers [8]. These parameters strongly affect the adsorption of the SPs onto lime particles thus modifying their effectiveness. Experimental results showed that the first polycarboxylate ether derivative, PCE1, was a star-shaped polymer, with a relatively short main backbone and long side chains, whereas the PCE2 was a worm-like polymer, with a longer main backbone and shorter side chains as compared with PCE1.

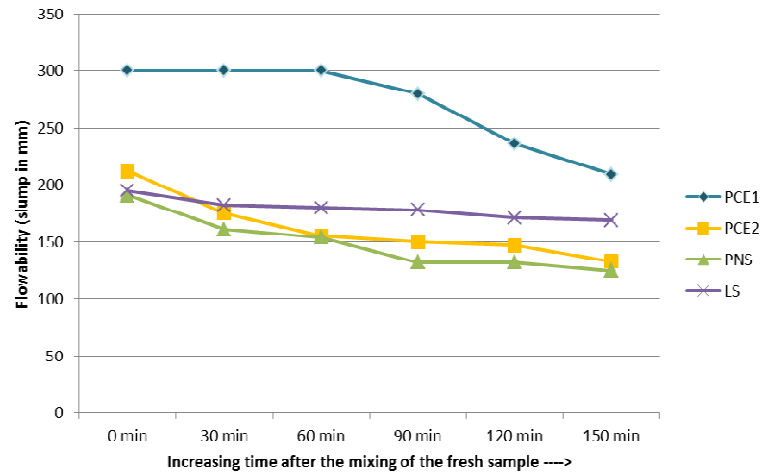


Fig. 2 Dispersing maintaining ability of pastes with 0.5 wt. % of SPs over time (min)

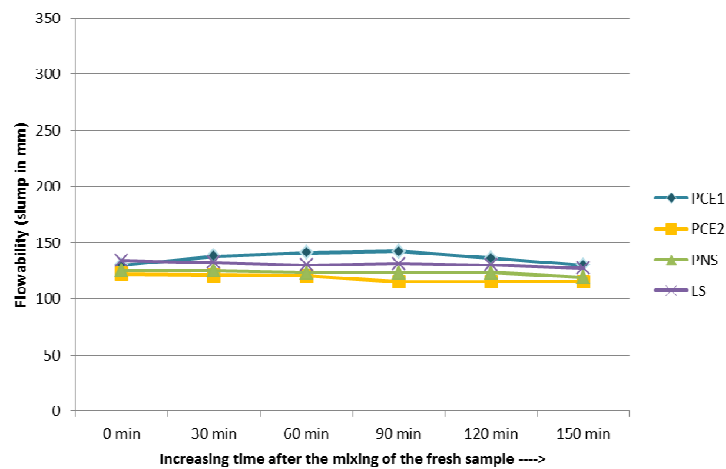


Fig. 3 Dispersing maintaining ability of pastes with 0.5 wt. % of SPs and 20 wt. % of NS over time (min)

Zeta potential studies can be used for assessment about the action mechanisms for the admixtures and the pozzolanic additives. For example, for PCEs, the progressive incorporation of NS caused a decrease in the zeta potential values, reaching values ca. +40 or +50 mV depending on the PCE used as titrant (Fig. 4). When the reactive NS was present, the pozzolanic reaction gave rise to the formation of C-S-H. Despite the reaction

between a compound with positive zeta potential (portlandite) and other with negative zeta potential (NS), the resulting products offered strongly positive values of zeta potential. The pozzolanic reaction compounds showed positive values of the zeta potential since the alkaline pH caused deprotonation of their silanol groups and the accumulation of multivalent counterions (mainly Ca^{2+}) in the electric double layer (EDL) gave rise to an overcharging that resulted in an apparent charge reversal (positive zeta potential). The adsorption interaction for the polycarboxylate-based superplasticizers may be explained by considering the positive zeta potential values of the C-S-H compounds in the lime media: the carboxylic functions located in the backbone of the tested copolymers appeared deprotonated and negatively charged at that alkaline pH, so that the electrostatic attraction would explain the adsorption of polycarboxylates. Adsorption isotherms showed that PCE2 was adsorbed in a 3- to 4-fold when compared with PCE1, in plain air lime samples. However, the overall zeta potential, ascribed to the EDL around CSH, was modified only to a limited extent, showing a high number of “inactive” sites and minor amount of polymer attached to CSH phases [8]. In spite of the low adsorbed amounts of PCE1, its dispersing action was higher because of its perpendicular adsorption, giving rise to a stronger steric hindrance.

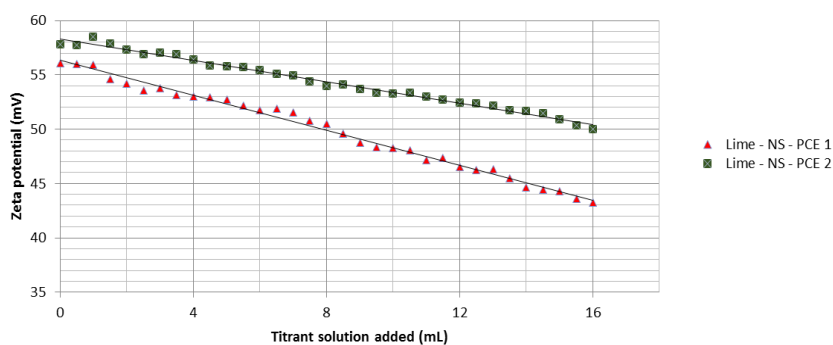


Fig. 4 Zeta potential of lime-NS pastes titrated with PCE1 and PCE2

For PNS, owing to its higher anionic charge density and to its linear shape, a flat adsorption has been proposed, whereas LS adsorption can be described as “perpendicular” to the surface of the particles (since this polymer shows a randomly branched molecular architecture) (Fig. 5). In the case of PNS, owing to its flat adsorption, the attached molecules could be surrounded by the growing carbonation/hydration products, yielding organo-mineral phases. This fact renders the attached molecules inactive, thus explaining the experimental results showing a lower dispersion effectiveness of this admixture and its really poor dispersion maintaining ability. These findings also point to the electrostatic repulsion as the main action mechanism to explain the PNS action, whereas the steric hindrance would be the main mechanism for LS.

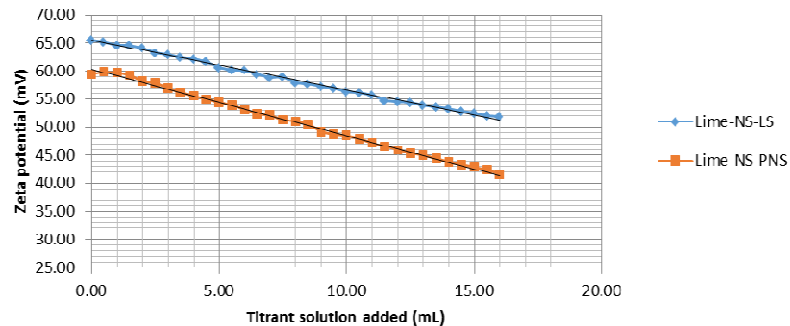


Fig. 5 Zeta potential of lime-NS pastes titrated with LS and PNS

Hardened state properties

Carbonation has a significant influence on the hardening process over time. Fig. 6 shows the compressive strength results after 7 and 91 curing days. The values of the samples S2, S4, S6 and S8 show the isolated influence of the SPs on the compressive strength for pure air lime mortars. However, the most outstanding improvements in mechanical strength were observed upon addition of both SPs and NS (samples S3, S5, S7 and S9), showing a clear synergistic effect ascribed to the filling effect of NS and the formation of CSH [6,9].

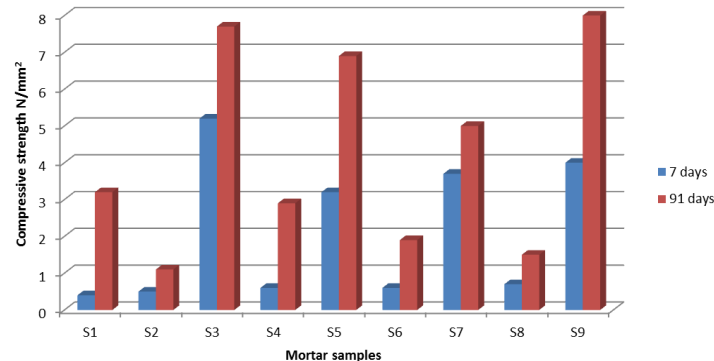


Fig. 6 Compressive strength values after 7 and 91 curing days

With respect to the values of the samples treated with either PNS or LS, the degree of carbonation accounts for the compressive strength results: the presence of LS clearly hindered the carbonation, as XRD, thermal analysis and FTIR studies showed. XRD phase evolution over time showed that the intensity of the main peak of the uncarbonated portlandite was larger in the presence of LS, while the amount of calcium carbonate (as calcite) was lower in comparison with the samples containing PNS. The presence of LS hindered the carbonation, resulting in higher amounts of Ca(OH)_2 and lower amounts of

CaCO₃. This fact took place in plain air lime samples as well as in NS–air lime samples. The degree of carbonation is higher in the case of the mortar containing the PNS-based plasticizer in comparison with the mortars containing LS (see in Fig. 7, comparatively, samples S1 with PNS or LS, samples, sample S6 vs. S8 and sample S7 vs. S9). Calcium silicate hydrates (CSH) were formed through the reaction between portlandite particles and reactive SiO₂ from NS [6]. CSH are preferentially formed in sample S9. The higher values of compressive strength of S9 at 7 and 91 days in comparison with S7 could be related to this fact (Fig. 6).

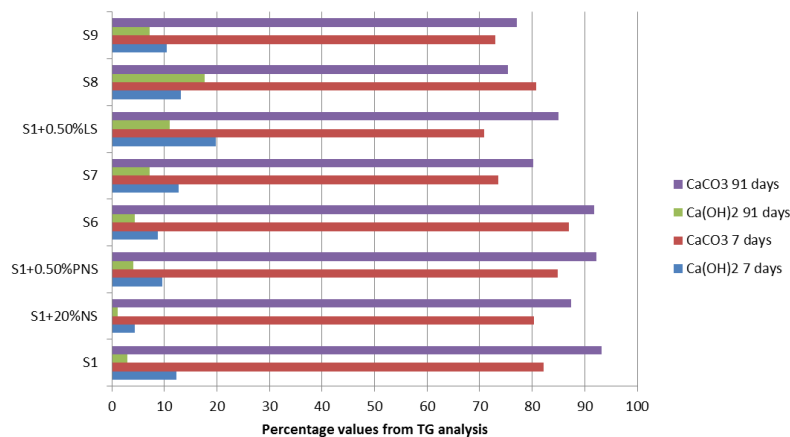


Fig. 7 Percentages of Ca(OH)₂ and CaCO₃ after 7 and 91 curing days calculated from TG results

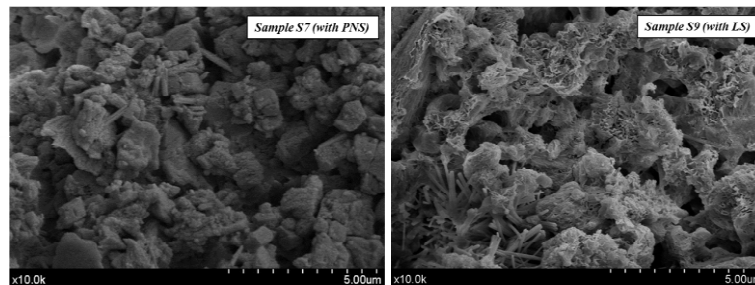


Fig. 8 SEM micrographs of mortars with NS treated with either PNS or LS

Microstructural examination carried out in hardened mortars by SEM also agrees with these conclusions. As an example, Fig. 8 depicts two micrographs of samples with 20% NS and 1% of PNS and LS, respectively, after 182 curing days.

It can be observed that in PNS samples the volume of carbonated lime is preponderant arising as agglomerations of calcite crystals [9]. Few C-S-H fibres can also be identified. However, in LS samples, some areas observed by SEM showed that the amount of carbonated lime areas is much lower, and the textural examination in these areas reveals a predominance of C-S-H compounds as the main hydration products, identified by their thin foil shape (sometimes resembling honeycomb structures) and a large agglomeration of C-S-H fibres, and confirmed by EDAX analysis [6].

Conclusions

The addition of the different superplasticizers admixtures produced a distinct behaviour in air lime mortars. Among the tested SPs, PCE1 turned to be the most effective in increasing the fluidity of the pastes and also showed the best dispersion maintaining ability over time. The molecular architecture of the polymer showed a great influence on this performance. In the case of polycarboxylates ethers, the large specific surface area of NS led to a large SPs consumption. NS provided a high number of inactive adsorption sites and polymers preferentially attached onto NS and not onto CSH. The flat adsorption of PNS and ulterior formation of organo-mineral phases reduced its efficiency in comparison with LS. The highest mechanical performance of the tested lime mortars was obtained under the combined action of both NS and SPs. In the comparative study between the PNS and LS-derived polymers, the rate of carbonation was higher when the former was part of the admixtures. However, the formation of CSH was preferred when the latter was added.

References

1. Bras A, Henriques FMA (2012), Natural hydraulic lime based grouts — the selection of grout injection parameters for masonry consolidation. *Constr Build Mater* 26: 135–14
2. Azeiteiro LC, Velosa A et al. (2014) Development of grouts for consolidation of old renders. *Constr Build Mater* 50: 352–360
3. Papo A., Piani, L (2004) Effect of various superplasticizers on the rheological properties of Portland cement pastes. *Cem Concr Res* 34: 2097-2101
4. Alvarez JI et al. (2013) Microstructural consequences of nanosilica addition on aerial lime binding materials: influence of different drying conditions. *Mater Charact* 80:36-49
5. Burgos-Montes O, Palacios M et al. (2012) Compatibility between superplasticizer admixtures and cements with mineral additions. *Constr Build Mater* 31:300-309
6. Fernández JM, Duran A et al. (2013) Influence of nanosilica and a polycarboxylate ether superplasticizer on the performance of lime mortars. *Cem Concr Res* 43:12-24
7. Chandra S, Björnström J (2002) Influence of superplasticizer type and dosage on the slump loss of Portland cement mortar – Part II. *Cem Concr Res* 32:1613-1619
8. Navarro-Blasco I, Pérez-Nicolás M et al. (2014) Assessment of the interaction of polycarboxylate superplasticizers in hydrated lime pastes modified with nanosilica or metakaolin as pozzolanic reactives. *Constr Build Mater* 73:1-12
9. Mo L, Panesar DK (2012) Effects of accelerated carbonation on the microstructure of Portland cement pastes containing reactive MgO, *Cem Concr Res* 42:769–777
10. Cizer O, Rodriguez-Navarro C et al. (2012) Phase and morphology evolution of calcium carbonate precipitated by carbonation of hydrated lime, *J Mater Sci* 47: 6151–6165