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Role of different superplasticizers on hydrated lime pastes and mortars

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Abstract

The behaviour of different superplasticizers admixtures was assessed for hydrated lime pastes and mortars. Sometimes, air lime pastes and mortars were modified with two supplementary cementing materials (SCMs), namely nanosilica (NS) and metakaolin (MK). Two different polycarboxylate ethers, a lignosulfonate and a naphthalene condensed sulfonate superplasticizer were added to lime pastes and mortars and their effects on fresh-state properties as well as on the mechanical strengths were evaluated. A close relationship was found between the molecular architecture of the plasticizers and the flowability of the pastes. Zeta potential assessment allowed us to elucidate the main action mechanisms for these admixtures. In the case of polycarboxylate ethers, the large specific surface area of nanosilica led to a large SPs consumption as compared with metakaolin with lower surface area. However, polycarboxylate ethers in MK-lime samples were attached favourably to the C-S-H and aluminate hydrates, so that the dispersing action was greater with respect to NS-lime suspensions.

Originality

The use of plasticizing admixtures in order to improve the handling of cement-based media has been extensively reported. High-range water reducers or superplasticizers (SPs) act by reducing the water demand and enhancing the flowability of the fresh mortars, yielding workable materials. So far little attention has been devoted to the study of the performance of superplasticizers in lime-bearing pastes and mortars. The widespread use of hydrated lime and pozzolan-hydrated lime pastes for paints, consolidant products, soil treatments and the obtaining of repair mortars and grouts, especially for architectural monuments of the Cultural Heritage, supports the interest of these materials. In order to design suitable hydrated lime pastes and mortars, the use of compatible and effective SPs seems to be imperative.

Keywords: *admixture; pozzolan; zeta potential; nanosilica; metakaolin.*

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1. Introduction

The use of plasticizing admixtures in order to improve the handling of cement-based media has been extensively reported (Navarro-Blasco I. *et al*, 2014). Superplasticizers (SPs) are frequently used for different goals: - to reduce the water demand in order to increase the strength of material, - enhance the flowability of the fresh mortar yielding workable materials. SPs with different compositions have been employed for these purposes: polycarboxylates (PCEs), lignosulfonates (LS), polynaphthalenes sulfonate-based (PNS) polymers, etc. (Papo A., Piani, L., 2004).

The presence of pozzolanic additives or supplementary cementing materials (SCMs), such as nanosilica (NS) and metakaolin (MK), could affect the interaction between the superplasticizers and the particles of the binder (Burgos-Montes O. *et al*, 2012; Fernández J.M. *et al*, 2013).

Remarkable enhancements have been observed after adding NS and/or MK into air-lime based pastes and mortars, as a result of their filler effect and the generation of calcium silicates hydrates (CSH) (Alvarez J.I. *et al*, 2013).

The performance of superplasticizers in lime-bearing pastes and mortars has not been widely studied (Navarro-Blasco I. *et al*, 2014). However, the use of compatible and effective SPs seems to be imperative in order to design suitable hydrated lime pastes and mortars, which could be used as repair mortars and grouts for architectural monuments of the Cultural Heritage.

The main aim of this work is to gain a better understanding on the behavior of different SPs in lime-bearing pastes and mortars modified some of them upon the addition of pozzolanic materials, such as NS and MK.

2. Materials and Methods

For the preparation of the samples, lime, aggregate and dry SPs admixtures were blended for 5 min using a solid admixtures mixer BL-8-CA. When necessary, MK as pozzolanic additive was added into the dry admixtures. Water (and, when required, the other pozzolanic additive as a NS suspension) was then added and mixed for 90 s at low speed, in a Proeti ETI 26.0072 mixer. Table 1 shows the mix proportions of the samples.

The determination of the fresh state properties was performed after 10 minutes to let the additives take effect. The consistency of the suspensions was assessed through the mini-spread flow test, by measuring the slump after the standardized procedure (EN 1015-3, 2000). The study of the interaction between the SPs and the lime and/or pozzolans (NS and MK) was performed by means of potential zeta's experiments in the solid/liquid interface. To this aim, suspensions with 7 g of lime and 25 g of either NS or MK per 140 ml of water were prepared and allowed to react for 30 minutes 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, 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 Fourier Transform Infrared – Attenuated Total Reflectance (FTIR-ATR) in a Nicolet-Avatar 360 instrument, and thermogravimetry – differential thermal analysis (TG-DTA) through a simultaneous TG-SDTA 851 Mettler Toledo

device. Compression strength tests were done on the two fragments of each specimen resulted from previous flexural tests, using on a Proeti ETI 26.0052 (rate of loading was 50 N/s).

Table 1 Mix proportions of the studied samples of lime mortars

Sample	Lime:aggregate ratio (by weight)	PCE1 (wt. %)	PCE2 (wt. %)	PNS (wt. %)	LS (wt. %)	NS (wt. %)
MP1	1:3	0	0	0	0	0
MP9	1:3	1	0	0	0	0
MP12	1:3	1	0	0	0	20
MP17	1:3	0	1	0	0	0
MP20	1:3	0	1	0	0	20
MP25	1:3	0	0	1	0	0
MP28	1:3	0	0	1	0	20
MP33	1:3	0	0	0	1	0
MP36	1:3	0	0	0	1	20

3. Results and discussion

3.1. Fresh state properties

In plain air lime-based mixtures, the presence of the four tested SPs increased the flowability (Figure 1). The value of flowability in the control group (MP1, admixture-free sample), with only lime and aggregate, is 173 mm. From these results, we can conclude that SPs act as water reducing agents that increase the fluidity of the fresh samples. Similar results were described for cement-based matrices (Chandra S., Björnström J., 2002). PCE1 turned to be the most effective in increasing the fluidity of the pastes (Figure 1). MP9 increased the slump values beyond the limits of the mini spread-flow test (> 300 mm). PNS-based polymer (MP25) also increased largely the fluidity. The slump values from sample MP25 underwent an increase of ca. 45 %.

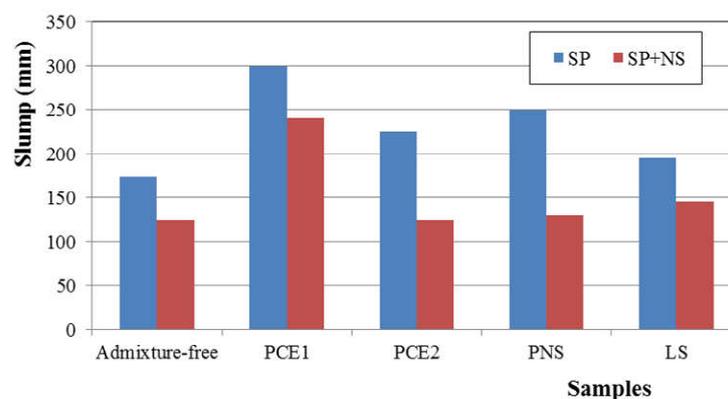


Figure 1 Slump values corresponding to the different admixtures.

The addition of NS provoked reduction in the values of fluidity in all the samples studied (Figure 1). This fact could be explained taking into account the small particle size of NS, which increase the water demand to achieve a similar consistency (Navarro-Blasco I. *et al*, 2014).

In other experiments performed in samples with PCEs and MK (Navarro-Blasco I. *et al*, 2014), the slump reduction in pastes was not as strong as in the case of the addition of NS, possibly due to the large particles size of the MK, which led to a lower water demand, and a certain lubricant effect, thus increasing the fluidity.

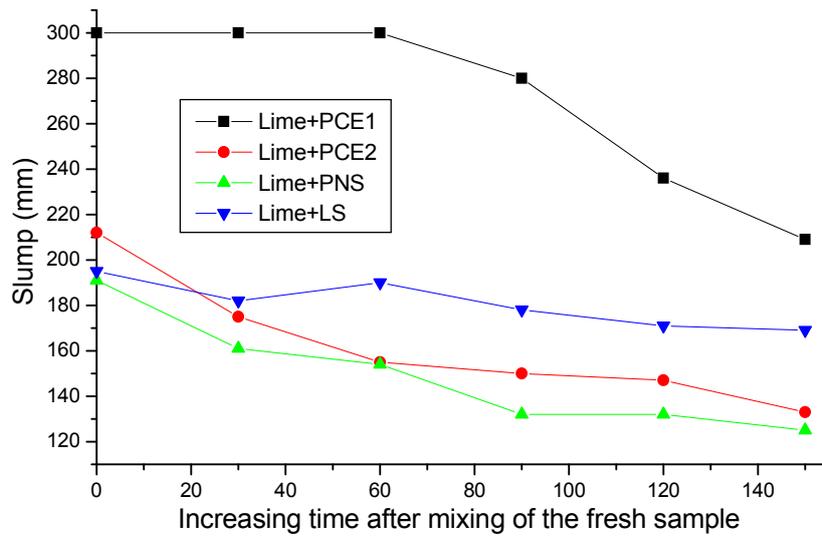


Figure 2 Dispersing maintaining ability of pastes with 0.5 wt. % of SPs over time (min)

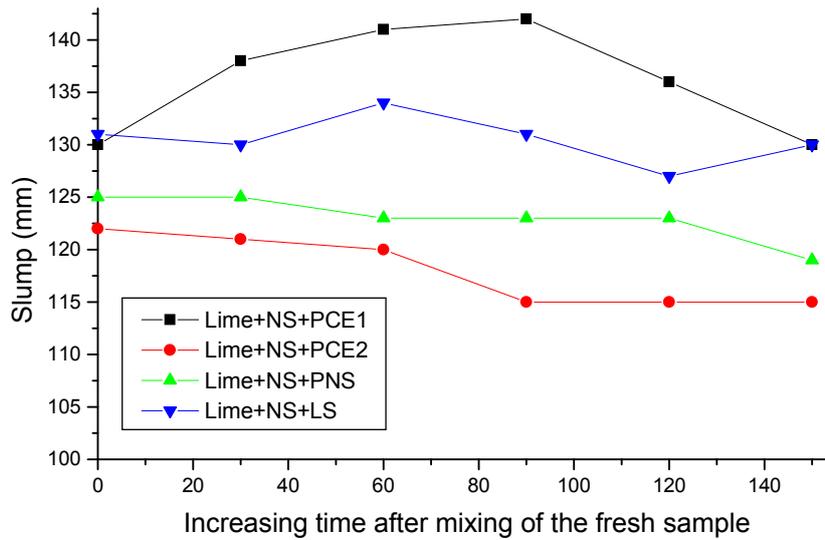


Figure 3 Dispersing maintaining ability of pastes with 0.5 wt. % of SPs and 20 wt. % of NS over time (min)

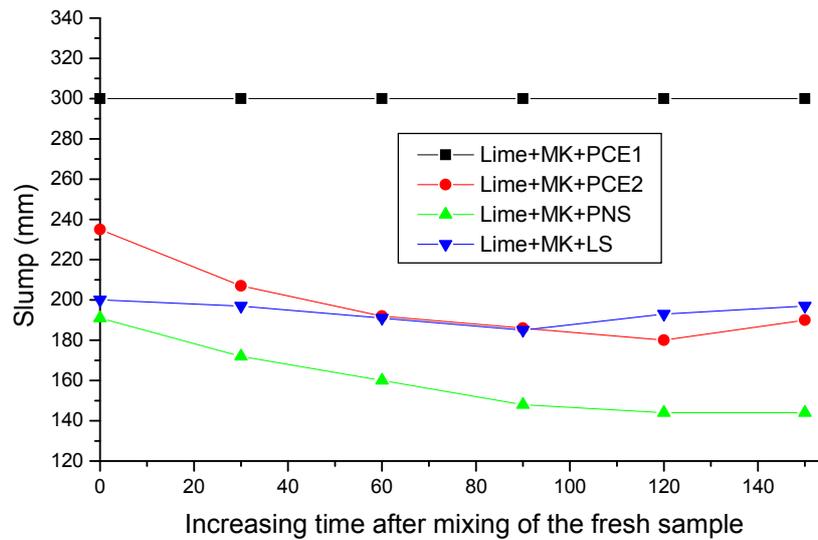


Figure 4 Dispersing maintaining ability of pastes with 0.5 wt. % of SPs and 20 wt. % of MK over time (min)

The dispersion maintaining ability over time of the pastes containing SPs (0.5 wt. %) and/or pozzolans (20 wt.% of NS or 20 wt. % of MK) was assessed by measuring the slump loss over time in minutes (Figures 2, 3 and 4). PCE1 showed the largest dispersing ability over time (Figures 2, 3 and 4). NS-bearing pastes offered low fluidity, reaching only values of slump between 115 and 142 mm (Figure 3). The different behavior of the SPs could be explained by their different molecular architecture of the polymers and their anionic charge densities (Navarro-Blasco I. *et al.*, 2014). These parameters strongly affect the adsorption of the SPs onto lime particles thus modifying their effectiveness.

Zeta potential studies can be used for assessment about the action mechanisms for the admixtures and the supplementary cementing materials (SCMs). For example, for PCEs, the most important reduction in zeta potential values from initial values (around + 60 mV) was measured for lime-MK pastes, reaching asymptotic values around +10 mV when 15 mL of PCEs were added as titrants (Figure 5). The decreasing of the values corresponding to the lime-NS pastes was minor, until reaching values ca. +40 or +50 mV depending on the PCE used as titrant (Figure 6). Specific surface area was one of the factors responsible for the differences in zeta potential and for the dispersing effectiveness in this system. Higher doses of SPs were required in lime-NS than in lime-MK to achieve similar flowability (Navarro-Blasco I. *et al.*, 2014). The large specific surface area of nanosilica (500 m²/g) led to a large SPs consumption as compared with metakaolin (20 m²/g) and could explain the higher consumption of SPs in this case. 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 (Navarro-Blasco I. *et al.*, 2014). The zeta potential values clearly decreased when MK-lime pastes were used, showing a large degree of plasticizing effectiveness. In MK-system, the polymer units preferentially anchored onto CSH and aluminate hydrates and not onto SCMs, as happened in the NS-system (Navarro-Blasco I. *et al.*, 2014).

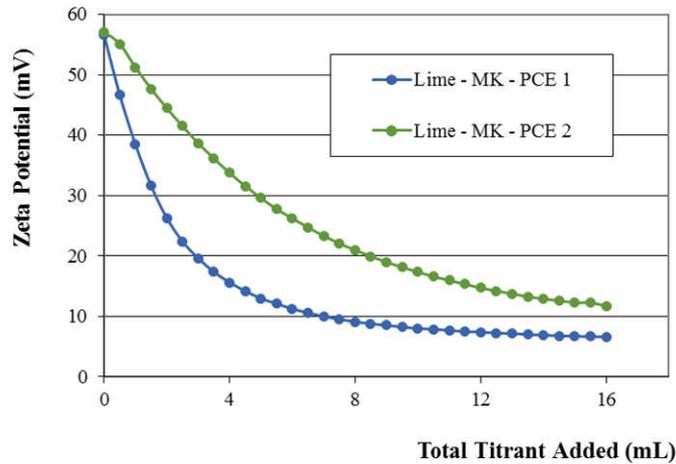


Figure 5 Zeta potential of lime-MK pastes titrated with PCE1 and PCE2

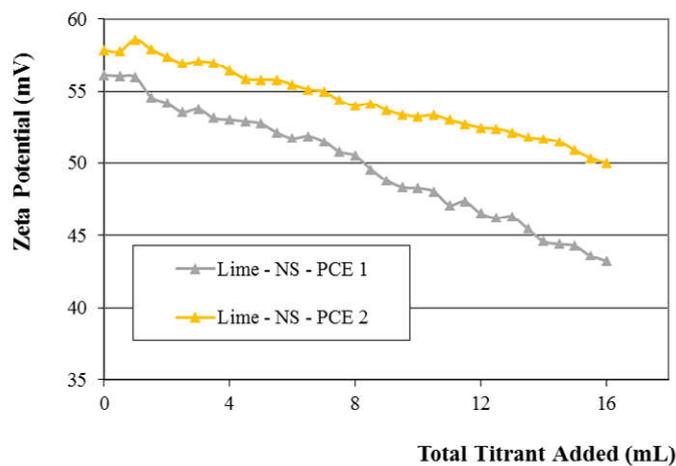


Figure 6 Zeta potential of lime-NS pastes titrated with PCE1 and PCE2

3.2. Hardened state properties

Carbonation has a significant influence on the hardening process in time. For all the samples, the highest values of compressive strength were obtained at 91 days (Table 2).

Table 2 Compressive strength results at 7 and 91 days (MPa)

Time	MP1	MP9	MP12	MP17	MP20	MP25	MP28	MP33	MP36
7 days	0.4	0.5	5.2	0.6	3.2	0.6	3.7	0.7	4
91 days	3.2	1.1	7.7	2.9	6.9	1.9	5	1.5	8

The isolated influence of the SPs on the compressive strength can be also observed in Table 2 for samples MP9, MP17, MP25 and MP33. The addition of 1 wt % of PCE2 (MP17) caused the highest strength increase at 91 days. The most outstanding improvements in mechanical strength were observed upon addition of both SPs and NS (samples MP12, MP20, MP28 and MP36), showing a clear synergistic effect (Table 2). These effects could be result of the filling effect of NS and the formation of CSH (Fernández J.M. *et al.*, 2013; Duran A. *et al.*, 2014).

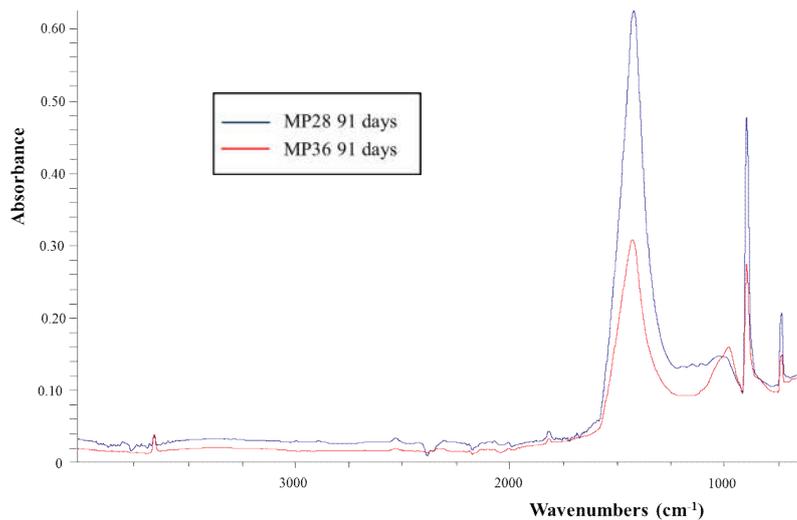


Figure 7 FTIR-ATR spectra corresponding to samples from mortars MP28 and MP36 after 91 days

Table 3 Percentages of $\text{Ca}(\text{OH})_2$ and CaCO_3 calculated from TG analysis at 91 curing days

Sample	$\text{Ca}(\text{OH})_2$	CaCO_3
MP28	7.21	80.13
MP36	7.25	77.11

The rate of carbonation and the formation of CSH at different curing times (mainly at 7 and 91 days) were followed by XRD, FTIR-ATR and TG-DTA, and will be elucidated in a further paper. By way of example, Figure 7 and Table 3 depict the infrared spectra and the percentages of $\text{Ca}(\text{OH})_2$ and CaCO_3 calculated from TG, corresponding to samples collected from MP28 (1 wt.% PNS + 20 wt.% NS) and MP36 (1 wt.% LS + 20 wt.% NS), both curing at 91 days.

The degree of carbonation is higher in the case of the mortar containing the PNS-based plasticizer (MP28) in whose infrared spectrum absorption bands corresponding to portlandite (the strong sharp signal at ca. 3650 cm^{-1} , characteristic of the O-H stretching vibration form of $\text{Ca}(\text{OH})_2$) (Legodi M.A. *et al.*, 2001) have practically disappeared whereas signals assigned to carbonate group (i.e. ca. 1400 cm^{-1}) have increased in comparison with the mortar containing LS (MP36) (Figure 7). The percentage of $\text{Ca}(\text{OH})_2$ in MP28 is minor, and the degree of carbonation is higher in this mortar due to the larger presence of CaCO_3 (Table 3). These results completely match with those derived from XRD.

Calcium silicate hydrates (CSH) were formed through the reaction between portlandite particles and reactive SiO_2 from NS (Fernández, J.M., *et al.*, 2013). The broad infrared band at around 1050 cm^{-1} can be associated with Si-O-Si asymmetric stretching vibrations derived from these compounds. CSH are preferentially formed in sample MP36 as observed in Figure 7. The higher values of compressive strength of MP36 at 7 and 91 days in comparison with MP28 could be related to this fact (Table 2).

4. Conclusions

The addition of the different superplasticizers admixtures produced a differential behaviour in pastes and mortars. PCE1 turned to be the most effective in increasing the fluidity of the pastes and also showed the best dispersion maintaining ability over time. In the case of polycarboxylates ethers (PCEs), the large specific surface area of NS led to a large SPs consumption as compared with MK with lower surface area. The dispersion performance was

more effective in the MK-lime suspensions, because of the polymer units preferentially anchored onto CSH and aluminate hydrates. NS provided a high number of inactive adsorption sites and polymers preferentially attached onto NS and not onto CSH.

The highest mechanical performance of the tested lime mortars was obtained under the combined action of both NS and PSs. 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.

5. Acknowledgments

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