



Laboratory of Building Materials
Department of Civil Engineering
Aristotle University of Thessaloniki

Proceedings of the
4th Historic Mortars Conference
HMC2016
10th-12th October 2016, Santorini, Greece

Editors

Ioanna Papayianni

Maria Stefanidou

Vasiliki Pachta



Proceedings of the 4th Historic Mortars Conference - HMC 2016
10-12 October 2016, Santorini, Greece

Editors

Ioanna Papayianni
Maria Stefanidou
Vasiliki Pachta

Published by

Laboratory of Building Materials
Department of Civil Engineering
Aristotle University of Thessaloniki

Thessaloniki, Greece, 2016

ISBN: 978-960-99922-3-7

The use of a lignosulfonate superplasticizer in repair air lime-metakaolin mortars

M. Pérez-Nicolás¹, A. Duran¹, R. Sirera¹, I. Navarro-Blasco¹, J.M. Fernández¹, J.I. Alvarez¹

¹ MIMED Research Group, Department of Chemistry and Soil Science, School of Sciences, University of Navarra, Spain, jalvarez@unav.es mimed@unav.es

Abstract: A superplasticizing admixture of natural origin, lignosulfonate (LS), was incorporated to air lime mortars sometimes modified with a pozzolanic additive, metakaolin (MK), to obtain a new range of repair mortars to be applied in Built Heritage. LS improved the flowability of the air lime samples and showed good slump retention over time: for example, after 150 minutes of the air lime pastes preparation, blends with LS lost only ca. 13% of the slump value. Experimental results showed that LS interfered with the carbonation due to its ability to form Ca^{2+} complexes. Adsorption isotherms and zeta potential measurements showed that LS was hardly adsorbed onto lime and C-S-H particles. Due to its branchy structure, LS exhibited an adsorption mechanism leading to steric hindrance as the main responsible mechanism for avoiding flocculation. The presence of free LS molecules in the dispersion was seen to improve the plasticizing effect of this polymer. Compressive strengths as well as the durability of these mortars exposed to freezing-thawing cycles were also determined to assess the applicability of these repair mortars.

Introduction

Lignosulfonate (LS) is used as superplasticizer in the field of binding materials for building purposes. The chemical structure of LS contains hydrophilic parts (such as sulfonic, methoxyl and hydroxyl groups) and a hydrophobic carbon chain (alkylbenzene) [1]. As superplasticizer, the incorporation of LS can cause a reduction in the water demand and enhance the flowability of the fresh mortar [2]. On the other hand, the presence of metakaolin as pozzolanic additive can alter the response of air lime based pastes and mortars as a result of their reaction with $\text{Ca}(\text{OH})_2$ yielding calcium silicate hydrates (C-S-H phases) [3] or aluminate-based compounds such as C_2ASH_8 and C_4AH_{13} [4]. Only a few works deal with the effect of superplasticizers in air lime-MK mortars. In some cases, a positive effect was found when other kind of superplasticizers (such as polycarboxylate

ethers) was incorporated together with a pozzolanic additive [1]: mechanical strength increases, enhancement of the durability and a porosity reduction. Therefore, the aim of the present work is to study the behaviour of air lime pastes and mortars including LS as superplasticizer admixtures and MK as pozzolanic additive.

Materials and methods

For the preparation of the samples, lime (CALINSA, Spain) of the CL 90-S class, limestone aggregate and dry LS admixture (0, 0.5 and 1.0 wt% with respect to the weight of lime) were blended for 5 min using a solid admixture mixer BL-8-CA. Water and MK as pozzolanic additive was added into the dry admixtures in different weight percentages (0, 6, 10 and 20 wt%) by weight of lime (bwol) and finally mixed for 90 s at low speed, in a Proeti ETI 26.0072 mixer. Table 1 shows the admixture proportions corresponding to the different samples. The equivalence of the 1:3 w:w ratio was 1:1 by volume.

Table 1. Mix proportions of the studied lime mortars

Sample	Lime:aggregate ratio (by weight)	LS (wt. %)	MK (wt. %)
MK1	1:3	0	0
MK2	1:3	0	6
MK3	1:3	0	10
MK4	1:3	0	20
MK13	1:3	0.5	0
MK14	1:3	0.5	6
MK15	1:3	0.5	10
MK16	1:3	0.5	20
MK17	1:3	1	0
MK18	1:3	1	6
MK19	1:3	1	10
MK20	1:3	1	20

Mortars were moulded in prismatic 40x40x160 mm casts, stored at 20 °C and 60% RH and demoulded after 7 days. Results at curing times of 7 and 91 days will be shown in this work.

The fresh state properties were determined after 10 minutes to let the additives take effect. Consistency of the pastes was obtained applying the mini-spread flow test at 0, 30, 60, 90, 120 and 150 min after being prepared, slump losses were also determined at these times. The zeta potential of the lime-LS and the lime-LS-MK samples was measured to understand the interaction between the superplasticizer and the lime and/or the cementing material (lime+MK). To this aim, suspensions with 7 g of lime and, when necessary, 25 g of MK per 140 mL of water were prepared and allowed to react for 30 minutes to ensure the pozzolanic reaction to take place. LS (1% w/v) solutions were used as titrants.

Suspensions formed by 5 g of lime and 6, 10 and 20 wt. % of MK (bwol) in 25 mL of water were prepared in order to carry out sorption experiments for LS. After stirring for 1 h and centrifugating at 8000 rpm for 15 min the samples, the supernatant was collected and filtered. The amount of LS adsorbed was determined by subtracting the initial and final concentrations of the LS in the solution, quantified by means of UV-vis spectrophotometry (maxima at $\lambda=285$ nm). Mathematical algorithms were used to estimate the adjustment of the data.

Compressive strengths were measured with a rate of loading of 50 N/s. Among the different methods to assess durability, resistance after the exposure to freezing-thawing cycles was tested, using a CARVELL 521-102 freezer. The cycles consisted of immersion of the samples for 24 h and freezing at -10°C for the following 24 h. To assess the durability of the samples, a qualitative evaluation based on visual appearance and general integrity of the samples was performed. The criterion was that followed in [5, 6].

Results and discussion

Fresh state characterization

Figure 1 shows the slump values of the samples, measured by the flow table test. In the control group (MK1), the flowability is 173 mm.

The incorporation of the superplasticizer caused a reduction in the water demand, enhancing the fluidity of the pastes (Figure 1). Similar results were described for matrices based in cements [7].

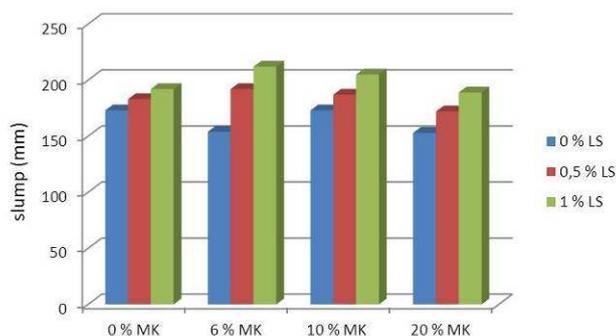


Fig. 1: Slump values for different air lime pastes

A higher amount of MK in air lime pastes with the same content of LS did not depict a clear dosage-response pattern. For low MK additions, a certain lubricant effect of MK seems to have taken place. A similar tendency has been reported when nanosilica as

pozzolanic additive were incorporated [1]. However, higher content in MK caused a decrease in the slump values.

The dispersion maintaining ability over the time of the fresh samples can be evaluated by measuring the slump loss over the time. Figure 2 shows the experimental fluidity loss during the first 150 min for lime pastes containing 0.5% LS and/or pozzolanic additive (20 wt.% MK). After 150 minutes of the air lime pastes preparation, blends with LS lost only ca. 13% of the slump value whereas samples with a combined presence of LS and MK lost hardly 1%; these small changes over time when MK and LS are incorporated are comparable to the performance reported for nanosilica as pozzolanic additive with other superplasticizers [1,8].

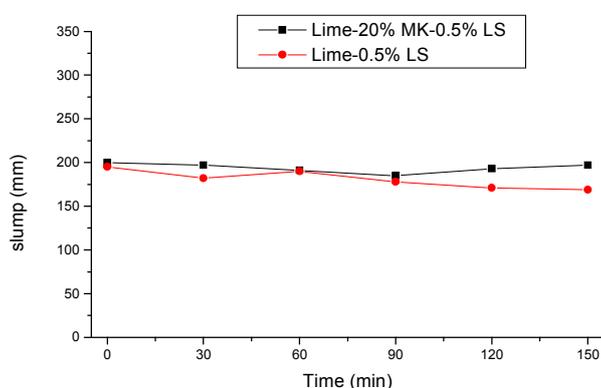


Fig. 2 Slump loss over time in air lime + MK pastes for LS

Zeta potential studies can be used for assessment about the action mechanisms of the admixtures and the MK. Changes in the zeta potential depend on the negative charge density of the polymeric molecules, on the amount of the adsorbed admixture and on the molecular architecture of the polymer that influences the type of adsorption and the subsequent displacement of the shear plane of the outer Helmholtz layer [1]. The lime dispersions start from positive zeta potential values, in good agreement with previous works [8-10]. Air lime particles offered positive values of the surface charge around +22 mV, ascribed to the zeta potential of the portlandite particles (Fig. 3) [1]. The progressive incorporation of the superplasticizer molecules reduced the zeta potential values as Fig. 3 shows. Sulfonate groups of LS are expected to be deprotonated at the alkaline pH of the lime media, conferring a negative charge to the polymers. In this way, some polymer molecules would be attached to the positive layer of the portlandite reducing the zeta potential. A high affinity of LS for Ca^{2+} complexation [11, 12] could justify the notable increase in zeta potential observed in Fig. 3 after the first LS adsorption.

On the other hand, air lime and metakaolin showed large positive values (ca. +60 mV, Fig. 4). In this case, the pozzolanic reaction is assumed to yield mainly C-S-H and C-A-H phases (negatively charged at alkaline pH owing to the silanol and aluminol groups deprotonation) that are strongly sheltered by a layer of Ca^{2+} counterions, resulting in a positive overcharging effect [13-16]. LS caused a progressive reduction of the zeta

potential, reaching asymptotic values around -20 mV when 15 mL of SP were added as titrant (Fig. 4).

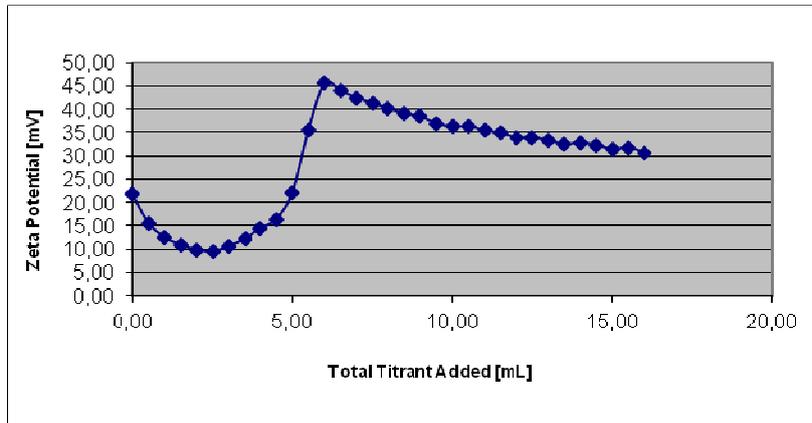


Fig. 3 Zeta potential of lime titrated with LS

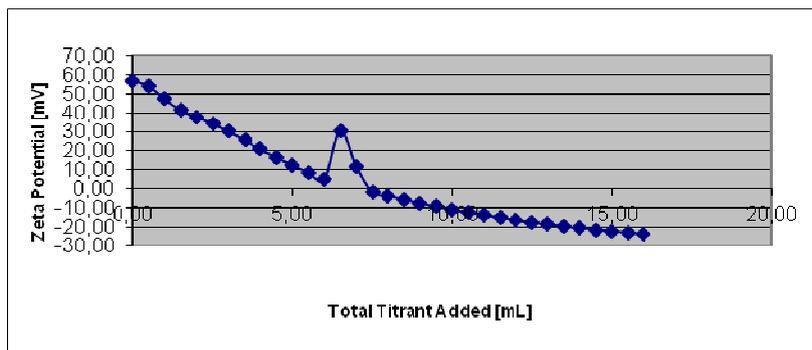


Fig. 4 Zeta potential of lime-MK titrated with LS

In the fresh state, adsorption isotherms of LS onto pure air lime, and a blended system LS-MK-air lime were assessed. Mathematical treatment of experimental adsorption data showed a better adjustment to a Freundlich model, which establishes a multilayer adsorption model (Table 2).

Table 2 shows a low adsorption when LS is added in the MK-lime system if it is compared with previous works concerning NS-lime system [1]. It has been published that the superplasticizer with a predominant mechanism based on steric hindrance and branchy structure was seen to be less adsorbed and more effective [1]. As it was aforementioned, LS yielded high slump values and presented a low slump loss over the time. In this sense, LS has been reported to easily form Ca^{2+} complexes [11, 12], avoiding some molecules to be attached to the portlandite or C-S-H or C-A-H particles. These “free” LS molecules in the interstitial solution may act as a steric hindrance to prevent particles from agglomeration, explaining a plasticizing action of this admixture [17].

Table 2 Results of adsorption isotherms onto air lime suspensions at different MK percentages: Langmuir and Freundlich adsorption parameters for LS

	Langmuir model			Freundlich model		
	qm	b	R2	K	1/n	R2
LS-lime-0%MK	32.10	0.00016	0.9509	0.01983	0.7812	0.9775
LS-lime-6%MK	28.74	0.00018	0.9242	0.01837	0.7830	0.9735
LS-lime-10%MK	31.48	0.00015	0.9647	0.01582	0.7977	0.9825
LS-lime-20%MK	29.05	0.00015	0.9400	0.01346	0.8076	0.9809

q_m: maximum sorption capacity, in mg g⁻¹.

b: the Langmuir constant, in dm³ mg⁻¹.

K (in mg^{1-1/n} dm^{3/n} g⁻¹), 1/n: the Freundlich constants.

R²: correlation coefficient of the linear regression

Hardened state characterization

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 3). The most accentuated improvements in mechanical strengths were observed upon addition of MK without LS (sample MK4) (Table 3). The formation of C-S-H and C-A-H phases would be responsible for this behaviour.

Table 3 Compressive strengths at 7 and 91 days (MPa)

Time	MK1	MK4	MK16	MK17	MK20
7 days	0.4	1.6	1.1	0.7	0.8
91 days	3.2	3.4	3	1.5	1.9

The rate of carbonation at 91 days was followed by TG-DTA. Table 4 depicts the percentages of Ca(OH)₂ and CaCO₃ calculated from TG, corresponding to samples collected from different MK and LS contents.

Calcium silicate and aluminate hydrates were formed through the reaction between portlandite particles and reactive SiO₂ and Al₂O₃ from MK. The degree of carbonation was helpful to understand these results: the presence of LS clearly hindered the carbonation, as thermal analysis showed (Table 4) resulting in higher amounts of Ca(OH)₂. This result justifies the minor values for compressive strength found for samples with this superplasticizer (Table 3). All these results prove that LS inhibited carbonation of the air lime mortars.

Table 4 Percentages of Ca(OH)₂ and CaCO₃ at 91 days, calculated from TG analysis

%	Ca(OH) ₂	CaCO ₃
MK1	2.96	93.14
MK4	1.15	92.50
MK16	9.16	78.34
MK20	11.90	78.90

The control group samples subjected to frost resistance test (freezing-thawing F–T cycles) underwent serious decay, in fact they were totally destroyed after just one cycle. This damaging effect of the F–T cycles in plain lime mortars is in good agreement with data reported elsewhere [6]. The incorporation of MK clearly enhanced the durability of the mortars in the face of these F–T cycles. It can be observed that samples with 20 wt.% MK can endure up to 24 F–T cycles. The presence of LS with MK was slightly detrimental for the durability of the samples, i.e. mortars with a 1% LS and 20% MK (MK20) suffered total destroy after 12 F–T cycles. A combined use of LS and MK in air lime mortars does not develop adequate resistance against freezing-thawing cycles, so that a dosage adjustment should be further studied.

Conclusions

The flowability of the fresh mortar improves after the incorporation of the lignosulfonate, which showed a large dispersing capability over the time. The values of slump were reduced when a higher amount of MK was added maintaining the LS content. LS was not highly adsorbed onto lime and C–S–H particles, being based its action mainly on steric hindrance.

The most emphasized enhancements in mechanical strengths and durability were observed upon addition of MK without LS, due to the pozzolanic reaction and formation of C–S–H and C–A–H phases.

Despite the better plasticizing action of LS, in air lime pastes and mortars with metakaolin, the use of LS should be carefully considered, since it hinders the carbonation compromising the mechanical strength.

References

1. Pérez-Nicolás M, Duran A et al (2016) Study on the effectiveness of PNS and LS superplasticizers in air lime-based mortars. *Cem Concr Res* 82:11-22
2. Ouyang X, Qiu X, Chen P (2006) Physicochemical characterization of calcium lignosulfonate—A potentially useful water reducer. *Colloids Surf A* 282–283:489-497
3. Vejmelková E, Keppert M, et al (2012) Mechanical, fracture-mechanical, hydric, thermal, and durability properties of lime–metakaolin plasters for renovation of historical buildings. *Constr Build Mater* 31:22-28

4. Rojas MF, Cabrera J (2002) The effect of temperature on the hydration rate and stability of the hydration phases of metakaolin–lime–water systems. *Cem Concr Res* 32:133-138
5. Lanas J, Sirera R, Alvarez JI (2006) Study of the mechanical behaviour of masonry repair lime-based mortars cured and exposed under different conditions. *Cem Concr Res* 36: 961-970
6. Duran A, Navarro-Blasco I, et al (2014) Long-term mechanical resistance and durability of air lime mortars with large additions of nanosilica. *Constr Build Mater* 58:147-158
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. 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
9. 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
10. Pointeau I, Reiller P et al (2006) Measurement and modeling of the surface potential evolution of hydrated cement pastes as a function of degradation. *J Colloid Interface Sci* 300:33–44
11. Uchikawa H, Hanehara S et al (1992) Effect of admixture on hydration of cement, adsorptive behavior of admixture and fluidity and setting of fresh cement paste. *Cem Concr Res* 22:1115–1129
12. Vikan H, Justnes H, Figi R (2005) Adsorption of plasticizers — influence of plasticizer and cement type. *Ann Trans Nord Rheol Soc* 13:127-134
13. Zingg A, Winnefeld F et al (2008) Adsorption of polyelectrolytes and its influence on the rheology, zeta potential, and microstructure of various cement and hydrate phases. *J Colloid Interface Sci* 323:301-312
14. Labbez C, Pochard I et al (2011) C-S-H/solution interface: experimental and Monte Carlo studies. *Cem Concr Res* 41:161–168
15. Jönsson B, Nonat A et al (2005) Controlling the cohesion of cement paste, *Langmuir* 21:9211–9221
16. Labbez C, Nonat A et al (2007) Experimental and theoretical evidence of overcharging of calcium silicate hydrate, *J Colloid Interface Sci* 309:303-307
17. Kim BG, Jiang S et al (2000) The adsorption behavior of PNS superplasticizer and its relation to fluidity of cement paste. *Cem Concr Res* 30:887