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Department of Civil Engineering
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Behaviour of air lime-metakaolin mortars modified with polynaphthalene sulfonate as superplasticizer

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Abstract: A new range of repair lime mortars were obtained by using as superplasticizer a polynaphthalene sulfonate-based polymer (PNS) and metakaolin as pozzolanic addition. Adsorption isotherms showed that PNS exhibited a high affinity for air lime particles with 52.08 $mg \cdot g^{-1}$ as maximum sorption capacity in pure air lime media. Mathematical treatment of experimental data showed an optimal adjustment to a Freundlich model, in which interactions arising from multilayer adsorption are taken into account. The experimental results suggested a great interaction of PNS with air lime media (pure air lime or air lime with MK). Zeta potential curves of air lime systems titrated with PNS showed a larger zeta potential reduction, giving rise to a charge reversal, as a consequence of the high anionic charge density of this polymer (2.44 meq of anionic $charge \cdot g^{-1}$). A flat adsorption was proposed as the attachment model of this admixture, owing to its higher anionic charge density and to its linear shape. The electrostatic repulsion was then the main action mechanism to explain the PNS function. In the hardened state, the combination of PNS and MK resulted sometimes in moderate mechanical strength increases and in a clear enhancement of the durability in the face of freezing-thawing cycles.

Introduction

The PNS is a polymeric molecule formed by condensation of naphthalene sulfonic acid and formaldehyde, in which the hydrophilic groups are mainly sulfonic groups, whereas the hydrophobic part is naphthalene. This compound has been widely used as a high-range water reducer or plasticizing admixture in cement and concrete samples, within the field of building materials [1]. Generally, plasticizers or so called superplasticizers (depending on their action capability) are organic molecules added in low percentages (usually below 0.5%) to fresh binding mixtures aiming to reduce the mixing water improving the fluidity [2].

For repair air lime mortars and grouts, these superplasticizers appear as potentially applicable admixtures with the purpose of keeping a good flowability of the plastic mixtures [3,4]. Of course, the reduction in mixing water would lead to an enhancement in the mechanical resistance as a consequence of a lower porosity. In addition, the simultaneous use of a pozzolanic additive, such as the well-known metakaolin, could yield mortars and grouts with suitable consistency, setting times and final mechanical strengths [5,6]. From the point of view of the scientists devoted to Built Heritage, the investigation on these issues broadens the knowledge about materials that could be applied for restoration processes.

It has been reported, in cement samples with PNS, the formation of organo-mineral compounds by the intercalation of superplasticizer molecules within the hydration products (mainly C-S-H phases). This fact gives, as a consequence, a severe consumption of the PNS in the early hydration stages [7-9]. In this contribution, the performance of air lime mortars modified with metakaolin and PNS as superplasticizer is described. PNS interaction and action mechanism is proposed and fresh and hardened state properties are assessed.

Materials and methods

Air lime mortars and pastes – when necessary – were obtained with calcitic air lime (CL90), aggregate and the required amounts of dry powdered admixture (PNS) and pozzolanic additive (MK). Dry components were blended for 5 min and afterwards mixing water was incorporated. Two different PNS proportions were tested: 0.5% and 1% w/w admixture/lime. With respect to MK, this additive was added in 0, 6, 10 and 20 wt.%. Therefore, we tested 9 different samples: P-MK1, control sample, of plain air lime mortar, P-MK2 (0% MK, 0.5%PNS), P-MK3 (6%MK, 0.5%PNS), P-MK4 (10%MK, 0.5%PNS), P-MK5 (20%MK, 0.5%PNS), P-MK6 (0%MK, 1%PNS), P-MK7 (6%MK, 1%PNS), P-MK8 (10%MK, 1%PNS) and P-MK9 (20%MK, 1%PNS). Fresh state properties were measured after 10 min to let the additives take effect. The mini-spread flow test (according to the flow table test) was used to test the consistency of the plastic samples. The zeta potential experiments allowed establishing the interactions between the admixture, the additive and the air lime particles in the solid/liquid interface. These interactions were studied in different dispersions of air lime and/or MK in which PNS (1% w/v) solutions were used as titrants. When the pozzolanic additive was incorporated, 30 minutes of reaction were allocated to guarantee the pozzolanic reaction between MK and air lime particles.

Fresh pastes were moulded in prismatic 40x40x160 mm, stored at 20 ºC and 60 % RH and demolded after 5 days. Samples were tested at different times: 7, 28, 91 and 182 days. Mechanical strengths were determined by flexural strength tests and compression strength tests. The later were done on the two fragments of each specimen resulted from flexural strength determination (rate of loading was 50 N/s). Total porosity and pore size distributions were carried out by mercury intrusion porosimetry (Micromeritics-AutoPoreIV-9500; pressure 0.0015 to 207 MPa). Among the different methods to assess durability, hardened mortars were subjected to different freezing-thawing cycles, analysing the decay degree after each one of the cycles.

Results and discussion

The values of the slump as a function of the contents of MK and PNS, respectively, can be observed (Fig. 1). In general, the presence of increasing amounts of MK gave rise to higher values of the slump, i.e. to higher fluidity of the fresh samples. MK exerted a certain lubricant effect, which allowed the particles to reduce their friction forces, thus increasing the fluidity [10]. The addition of PNS also increased the flowability of the samples, depicting a clear dosage-response pattern.

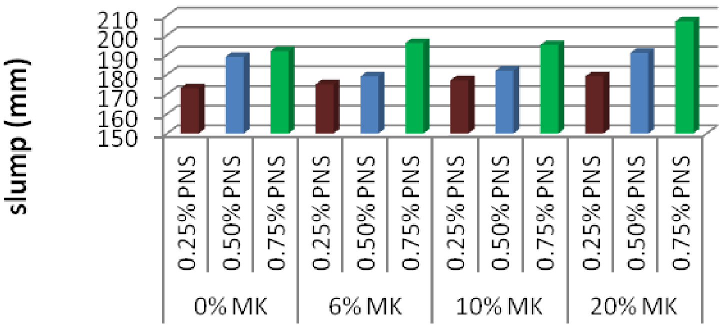

Fig. 1 Slump values corresponding to the different mortars according to the wt.% of MK

The dispersion maintaining ability over the time, also called slump loss, has been revealed as one of the most important characteristics of the efficiency of superplasticizers. In this case, this property was evaluated by assessing the slump loss over the time. The experimental results can be observed in Fig. 2, which shows the fluidity loss over the first 150 min after the mixing for air lime pastes with PNS and with PNS+MK, for 0.5 wt.% dosage of the superplasticizer. Results are similar for both compositions and showed, in general, a poor dispersion maintaining ability of the tested admixture, since in the case of air lime samples with PNS, the slump values almost reached the minimum slump value. This fact can be strongly related to the adsorption of this admixture and to the formation of organo-mineral, inactive compounds. This fact has been reported in cement samples treated with PNS, suggesting a delayed addition for this admixture, i.e., the mortar preparation should involve a first step of mixing with water and, after 30 min, the incorporation of the PNS superplasticizer, in order to avoid an intense consumption and poor effectiveness of the polymer during the first stages.

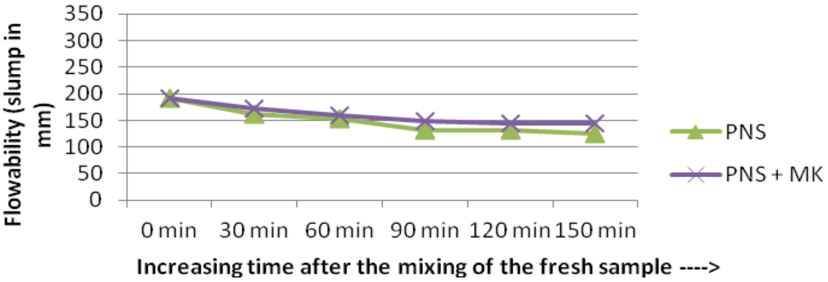

Fig. 2 Slump loss vs. time for samples treated with PNS or with PNS+MK

Adsorption isotherms were carried out to measure the affinity of the PNS for the air lime particles or for the system MK-air lime. It has to be noticed that, owing to the high speed of the pozzolanic process, a quick formation of the C-S-H and C-A-H could be reasonably expected in the system, so that the adsorption of the PNS would take place preferentially on these compounds in the presence of MK. Fig. 3 depicts the adsorption isotherms, showing a similar pattern for all the compositions. PNS was strongly retained in the tested binding media, behaving in a similar way to that described for cement media. A high consumption of this admixture is then expected. Fig. 4 shows the adjustments of data to different sorption models: Freundlich model, in which interactions arising from multilayer adsorption are taken into account, yielded the best adjustments. Mathematical treatment of experimental data showed that, according to a Langmuir adjustment, the adsorption of PNS onto lime particles was the highest, showing a scarce reduction in the presence of MK (q_m values, maximum sorption capacity, were 51.23 mg g^{-1} for plain lime and 44.7 mg g^{-1} for lime+20wt.% of MK).

Regarding the setting time (values collected in Fig. 5), it can be seen that the addition of the PNS delayed the setting of the mortars, showing a dosage-response pattern: the higher the amount of PNS, the stronger the delay in the setting time. The delay in the setting of binding materials is a very frequent problem that arises when using superplasticizers. In this case, however, the delay was not as important as in some other cases reported in the literature [5, 6]. On the other hand, the increasing amounts of MK also resulted in delayed setting, in line with the effect of other pozzolanic additives, like nanosilica [11].

Zeta potential experiments were carried out with the aim of assessing the interaction mechanism of the PNS in air lime+MK systems. Fig. 6 depicts the zeta potential pattern of dispersions of air lime + MK vs. increasing amounts of PNS. The dispersions start from positive zeta potential values: literature has reported that air lime particles offered positive values of the surface charge around + 20 mV [12]. In the presence of MK, the pozzolanic reaction between portlandite and MK is expected to result in the formation of C-A-H and C-S-H compounds, usually with a negative superficial charge at the alkaline pH of the lime media, which causes deprotonation of the silanol and aluminol groups. Nevertheless, this strong negative superficial charge is strongly sheltered by a layer of Ca^{2+} counterions, resulting in a charge reversal phenomenon [13]. Due to the alkaline pH, sulfonate groups of PNS are also deprotonated, yielding a negative charge. Progressive adsorption of the polymer onto the cationic double layer of the particles caused a decrease of the zeta potential, even beyond the isoelectric point.

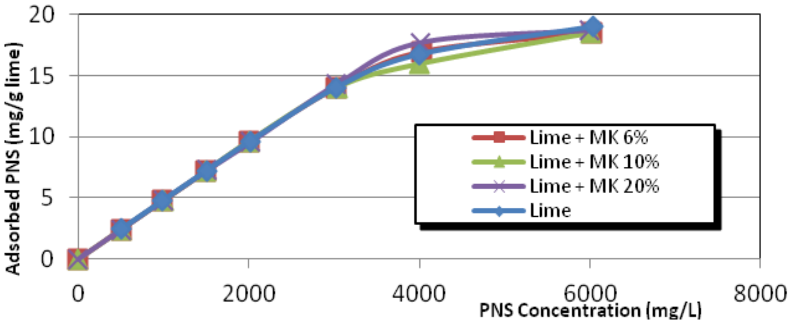

Fig. 3 Adsorption isotherms of PNS onto lime with MK at different percentages

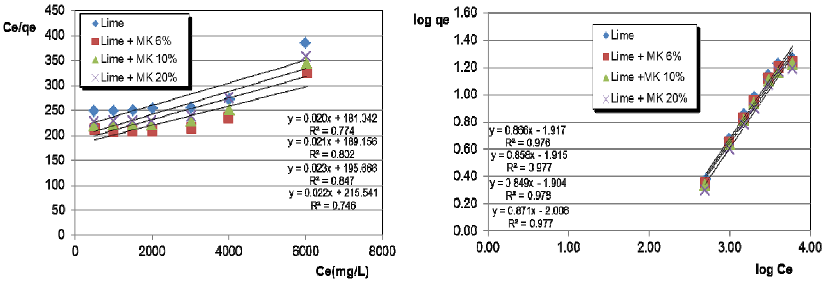

Fig. 4 Langmuir (left) and Freundlich (right) adjustments of the PNS adsorption experiments (C_e: concentration and q_e amount of PNS sorbed after each equilibrium point)

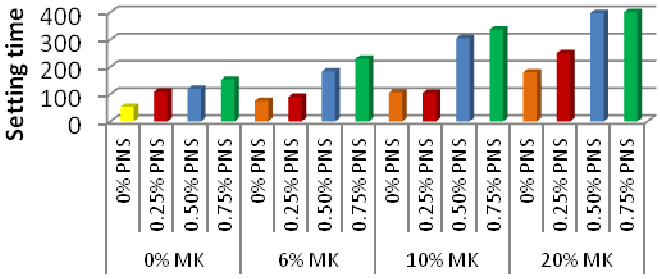

Fig. 5 Setting time (min) of the different mortars according to the wt.% of MK

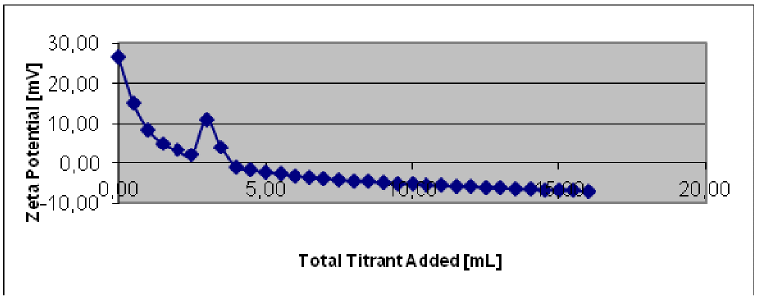

Fig. 6 Zeta potential of lime+MK pastes vs. increasing dosages of PNS

These findings are also supported by the expected flat adsorption of the polymer [9] as a consequence of its molecular architecture and its strong anionic charge density (2.44 meq of anionic charge per g of polymer). Finally, the zeta potential evolution shows, in good agreement with the adsorption isotherms, that PNS strongly interacts with air lime + MK media, although negative values of the system are not very marked, reducing its impact in terms of dispersing efficiency. The dramatic initial decrease in the zeta potential was followed by a mitigated decrease, showing that the formation of organo-mineral compounds and/or the predominance of the electrostatic repulsions as dispersion mechanism did not favour the effectiveness of the PNS. This fact matches well the poor dispersion maintaining ability of PNS previously discussed.

With respect to the mechanical strengths of the treated mortars, both flexural as well as compressive strength results (Fig. 7 and Fig. 8) showed the positive effect of the combination of the pozzolanic additive, MK, with the PNS. Especially regarding the compressive strengths, it can be seen that the incorporation of 20% of MK resulted in a noticeable increase in the strength, although the combined presence of 0.5 wt.% of PNS (P-MK5) improved the final resistance.

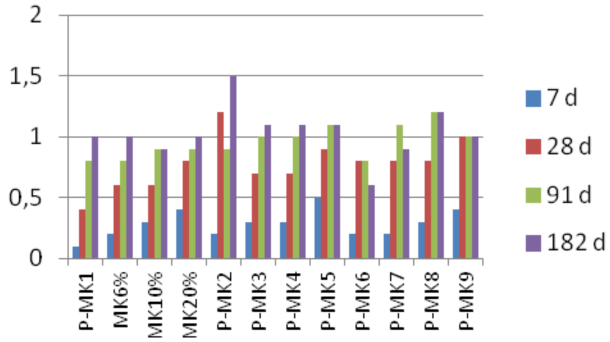

Fig. 7 Flexural strengths (MPa) of samples at different curing days

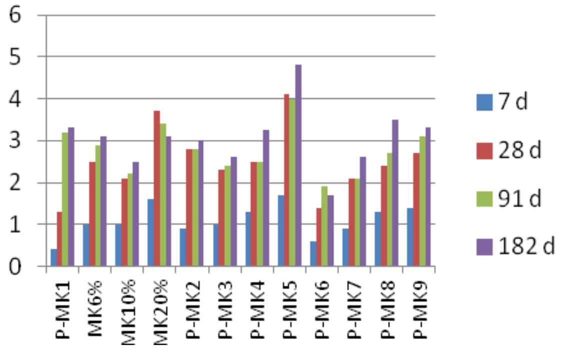

Fig. 8 Compressive strengths (MPa) of samples at different curing days

The pozzolanic reaction between MK and portlandite as well as pore size distribution of these mortars accounted for this finding (Fig. 9): the simultaneous presence of PNS and MK caused a reduction in the main pore size (from 0.9 µm, in sample P-MK1 to 0.6 µm and 0.55 µm in samples P-MK5 and P-MK9).

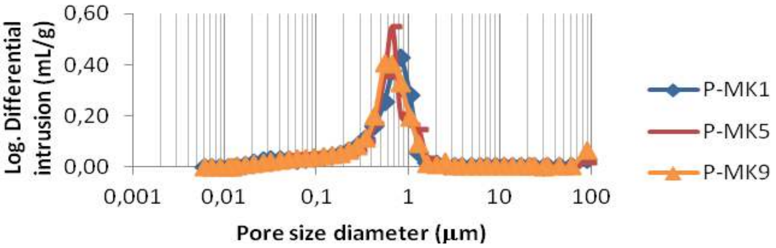

Fig. 9 Pore size distributions of different mortars after 182 curing days

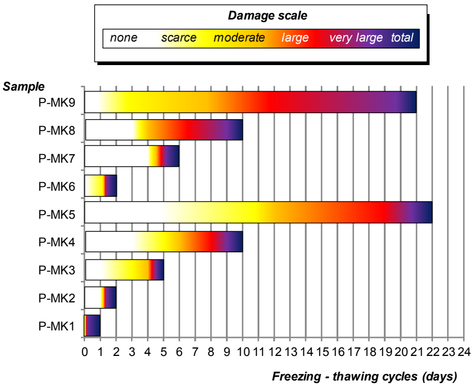

Fig. 10 Freezing-thawing resistance of the tested mortars

Durability of these mortars was studied by means of freezing-thawing resistance in continuous cycles after the total destruction of the specimen (degree 5 of alteration). Fig. 10 shows that the combination of MK and PNS outstandingly increased the durability of the mortars, withstanding until 22 freeze-thaw cycles.

Conclusions

The incorporation of PNS increased the slump of the air lime + MK samples, although PNS showed a poor dispersion maintaining ability. As in the case of the cement-based materials, a delayed addition should be further studied and considered for air lime-based mortars and pastes. The flat adsorption of PNS and ulterior formation of organo-mineral phases seems to be responsible for this behaviour. Adsorption isotherms revealed a high consumption of this admixture in air lime + MK samples. A positive effect of the combination of PNS and MK was found in terms of mechanical strengths as well as durability after the exposure to freezing-thawing cycles.

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