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Long-term mechanical resistance and durability of air lime mortars with large additions of nanosilica

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HIGHLIGHTS

- NS in large amounts showed an outstanding pozzolanic activity and filler effect.
- The superficial cracking was minimised owing to the reduction of the drying shrinkage.
- Increase in long-term strength was found for samples with large additions of NS.
- Sulfate attack damaged mortars due to the formation of calcium sulfate and thaumasite.
- Large NS percentage improved the lime mortars durability delaying the decay evolution.

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ABSTRACT

The performance of air lime mortars modified by the incorporation of large amounts of nanostructured colloidal silica–nanosilica, NS – (6, 10 and 20 wt.% with respect to lime) was the main objective of this work. Fresh mixture properties (water demand, setting time and plastic shrinkage), mechanical strengths up to one year and specimens' durability after accelerated ageing conditions (climatic chamber, freeze–thaw cycles and sulfate attack by $MgSO_4$ corrosion test) were evaluated. NS was seen to have a strong pozzolanic activity in air lime media. Although the addition of NS gave rise to an increase in volume contraction, the superficial cracking caused by the drying shrinkage was reduced. A noticeable increase in the compressive strength values was observed in the NS-bearing mortars owing to the NS filler effect and the C–S–H formation, as proved by SEM examination and MIP analysis. A honeycomb-shaped network of C–S–H phases appeared as the prevailing microstructure in mortars with large NS additions. In the face of accelerated ageing processes, the presence of NS made the mortars more durable, delaying the progress of decay.

1. Introduction

Nanotechnology can be defined as the science of controlling the properties at nanometer scale which can make revolutionary changes in bulk materials' properties [1]. Potential improvements brought about by using nanoparticles, carbon nanotubes and nanofibers to increase the strength and durability of cementitious composites have been researched [2,3].

Among nanostructured materials, nanosilica (NS) – a suspension of amorphous colloidal silica – has drawn the attention of several researchers because, in cement-based materials, it has shown an outstanding packing ability and pozzolanic activity [4–7]. The small size of NS particles allows them to act as a filler, taking up the voids in the cement composites, thus reducing porosity and enhancing mechanical performance. In addition, the occurrence of a pozzolanic reaction between NS and $Ca(OH)_2$ present in the cement media yields C–S–H compounds that improve the cohesiveness and strength of the matrix.

Furthermore, the interest of lime-based materials to use to repair works of historical monuments or for rendering mortars can be easily inferred from the growing number of studies dealing with this kind of mortar. Although the role of other pozzolanic additives, e.g. metakaolin, in lime-based mortars, has been widely researched [8–14], few efforts have focused on the performance of lime-based materials modified by the addition of NS [15,16]. In previous works dealing with either lime-based or even cement-based materials, the incorporation of NS was limited to relatively low amounts (around 1–5% by weight of binding material) [15,17–19]. The main objective of the present study is to gain knowledge about the

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behaviour of air lime mortars modified by the incorporation of large amounts of NS (6, 10 and 20 wt.% with respect to lime). Water demand and setting time were evaluated in the fresh mixtures. Additionally, the long-term mechanical resistance was assessed, as well as the durability of the NS-lime mortars in the face of accelerated ageing conditions (climatic chamber, freeze–thaw cycles and corrosion test with magnesium sulfate).

2. Materials and methods

2.1. Materials

Mortars were prepared taking as binder a dry slaked lime (class CL 90-S according to the European norm [20], supplied by CALINSA). The employed aggregate was a calcitic sand, class AF-T-0/1-C according to norm [21], supplied by Caleras de Liskar (CTG group). The chemical and mineralogical characteristics of the raw materials, and also their grain size distributions, have been reported previously [22]. A colloidal silica suspension supplied by ULMEN Europa S.L. was used as NS. This suspension showed a solid/liquid ratio of 0.28 and pH = 9.68. Spherical morphology and size of NS particles were provided by TEM examinations as depicted in Fig. 1 [16].

The selected binder/aggregate ratio was 1:1 by volume (1:3 by weight) in accordance with previous studies showing a good performance for this mixture proportion [23]. The water quantity was optimized for the fresh mixtures of the control group in order to obtain a suitable mortar consistency. The workability of the control mortar without NS was considered optimal when the slump in the flow table test was maintained in the range of 175 ± 5 (173 mm), which was reached with a water to lime ratio of 1.12. This same ratio was kept constant for all the batches of samples, with the aim of assessing the effect of NS addition on the water demand and workability of the fresh mixtures.

Four different batches of samples were prepared as a function of the amount of NS: PZNS-L0, as a control group with 0 wt.% NS, PZNS-L6 (6 wt.% NS with respect to the lime weight), PZNS-L10 (10 wt.% NS) and PZNS-L20 (20 wt.% NS).

2.2. Mortar preparation

Lime and sand were blended for 5 min in a BL-8-CA (Lleal S.A.) solid mixer. Afterwards, water – and when necessary, the selected amount of NS suspension – was added and mixed with for 90 s at low speed in a Proeti ETI 26.0072 mixer. The required amount of fresh mixture was then used for the fresh-state tests, as described below.

For measurement of the properties at hardened state and durability, mortars were molded in prismatic 40 × 40 × 160 mm casts, stored indoors at 60% RH and 20 °C, and de-molded 5 days later [24]. Different curing times were set: 7, 28, 91, 182 and 365 days, and three specimens of each mortar were tested at each curing time in order to make the results representative.

Specimens for durability tests were cured for 56 days under the above mentioned curing regime before being subjected to the different assays.

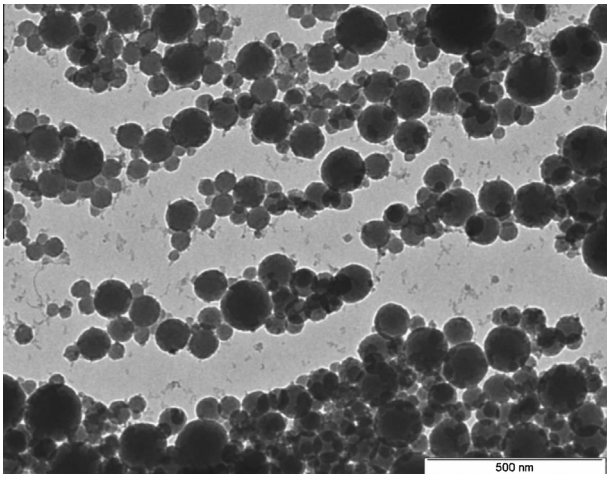

Fig. 1. TEM examination of the colloidal suspension of NS.

2.3. Experimental methods

2.3.1. Tests on fresh mixtures

For measuring the fresh state properties, mortars were allowed to settle for 10 min. Afterwards, by means of standardized tests, several properties were measured: consistency [25], air content [26] and, as a way of estimation of the setting time, workable life [27].

2.3.2. Tests on hardened samples

In hardened samples, at each curing age, the compressive strength experiments were executed on a Proeti ETI 26.0052, the rate of loading being 50 N s^{-1}. By means of mercury intrusion porosimetry (MIP), using a Micromeritics AutoPore IV 9500 porosimeter (pressure range between 0.0015 and 207 MPa), the pore size distributions of the fragments of the samples were obtained. When deemed necessary, samples were manually ground in an agate mortar, so that a complete characterization of the powdered mortars was executed by X-ray diffraction (XRD) (Bruker D8 Advance diffractometer with a Cu Kα1 radiation and and a step size of 0.04° and a time per step of 1s, from 2° to 80° (2θ) and Fourier Transform Infrared-Attenuated Total Reflectance (FTIR-ATR) (Nicolet-Avatar 360, resolution of 4 cm^{-1}). A simultaneous TG-SDTA 851 Mettler Toledo device allowed us to establish the thermal behaviour of the samples under the following conditions: alumina crucible, 10 °C min^{-1} heating rate, from ambient temperature to 1000 °C, static air atmosphere. The textural examination of the mortars' microstructure was carried out through a Hitachi S-4800 scanning electron microscope (SEM), coupled to an EDS detector. Before SEM–EDS analysis, samples were coated with gold films. Shrinkage assessment was obtained by measuring with a gauge the length variation of a prismatic sample of each one of the mortars at different curing days: 1, 3, 7, 14 and 28 days.

Table 1
Steps of the ageing cycle in the climatic chamber.

Step	T (°C)	RH (%)	Rain	UV light	Time (h)
1	35	30	–	–	12
2	45	20	–	✓	12
3	12	95	✓	–	1
4	12	95	–	–	4.5
5	12	95	✓	–	1
6	12	95	–	–	4.5
7	12	95	✓	–	1
8	−5	0	–	–	12

Table 2
Fresh state properties.

Sample	Flowability (flow measured by slump in mm)	Air content (%)	Setting time (min)
PZNS-L0	173	3.2	215
PZNS-L6	167	3.4	980
PZNS-L10	146	3.2	494
PZNS-L20	126	3.4	208

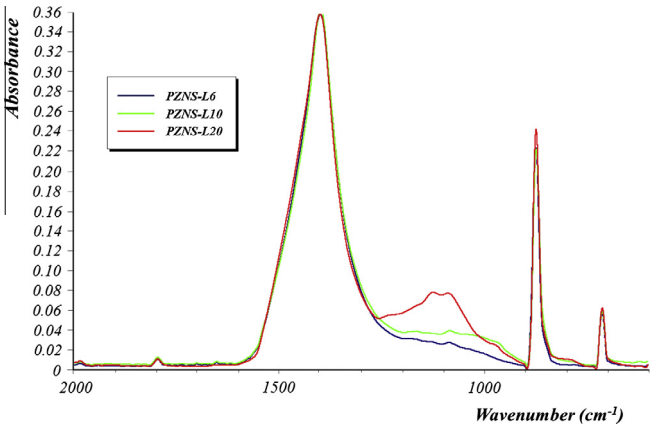

Fig. 2. FTIR spectra of the samples with NS.