Assessment on the performances of air lime-ceramic mortars with nano $\text{Ca}(\text{OH})_2$ and nano SiO_2 additions

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ABSTRACT

This research presents a novel approach based on the combination of nanotechnology and Roman technology by investigating how adding nano $\text{Ca}(\text{OH})_2$ and nano SiO_2 modify the performance of air lime mortars containing Roman ceramics. Microstructural, physico-mechanical properties were periodically controlled until 120 days of curing. XRD and TGA analyses showed that adding nano SiO_2 either alone or with nano $\text{Ca}(\text{OH})_2$ were more beneficial to improve the pozzolanic activity in the mortars. The less stable hydrated phases generated led to microcracks which eventually impaired compressive strength but enhanced deformability capacity. These results provide insight into the development of highly compatible mortars for cultural heritage.

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1. Introduction

Before the discovery of Portland cement, lime-based mortars and plasters have been widely used in masonry buildings. Lime-based mortars present important properties such as their moderate mechanical properties, their low modulus of elasticity together with the optimal water vapour permeability performance and their outstanding durability [1–4]. However, the slow setting and carbonation times as well as the high drying shrinkage are well-known disadvantages of using lime as binder in mortars [5]. Thereby, its use was gradually replaced by cement which has several advantages over it (mainly its quick set time and low cost). Nonetheless, the use of cement as binder has received considerable critical attention in historic building restorations due to its incompatibility with the ancient masonry [6,7]. Thus, in recent years, there has been a renewed interest in lime-based mortars for restoration purposes [6–10]. Finding new additives to improve specific lime mortar properties has become a major concern among researchers in this field [1,8,11–13].

The addition of organic and inorganic materials to lime based mortars has been a practice widely used since antique times [12]. Different studies have evidenced the use of natural pozzolans (e.g. materials of volcanic origin, calcined clays, and ashes of organic origin, among others) as additives in historic lime mortars to provide imperviousness and strength [2,3]. However, as they were not always available, ceramic fragments and powder were used instead [4,11]. The hydraulic performance induced in lime-based mortars by the addition of silicon-based ceramics is responsible for the good quality and mechanical properties of the mortars, as well as an enhanced durability [14]. Those mortars had been reproduced by different researchers [11,13–16]. These studies reported that the reaction that occurs when low temperature fired ceramics are kneaded with $\text{Ca}(\text{OH})_2$, in the presence of water and atmospheric CO_2 , generates hydrated calcium silicates and aluminates, which give the final resistance to the mortar.

On the other hand, recent research has paid increasing attention to the use of nanoparticles (NPs) in mortars for improving their short-term performance, and consequently their properties. Significant progress has been reached with the development of both organic (e.g. silicon-based polymer nanocomposites) and inorganic nanomaterials (e.g. calcium and magnesium hydroxide and metal oxide nanoparticles) [17,18]. Their unique physical and chemical characteristics, mainly their high-surface area and consequently their high reactivity, may

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beneficially modify the mechanical properties and the durability of the mortars. Most of these studies have focused on cement-based mortars to improve its durability and sustainability [19–21]. In air lime mortars, novel functionalities based on photocatalytic properties were reported by the addition of titania (TiO_2) nanoparticles [22–24]. These authors confirmed an improved hydration and carbonation rate. More recently, multifunctional silver-doped TiO_2 nanoparticles have also been reported as additive in lime-based mortars to give them improved photocatalytic and antimicrobial properties [25]. However, amongst all available nanomaterials calcium hydroxide (Ca(OH)_2), commonly named as nanolime, and nanosilica (SiO_2) are the most widely used in the conservation field.

The action of nanolime is generally based on the carbonation reaction, when it is in contact with the atmospheric CO_2 in humidity conditions, occurring with the consequent pore filling by the precipitation of CaCO_3 . Therefore, it has been widely used as consolidating agent for various kinds of stone materials [17,26,27], wall painting [18] and lime mortars [28–30]. On the other hand, nanosilica provokes pozzolanic reactions and acts as fillers in the lime binder, resulting in a positive effect on compressive strength [1,31]. These nanoparticles have been previously examined in cement mortars [32], as well as in air lime mortars [33]. This latter reported the generation of microstructural modifications into mortars by the addition of SiO_2 NPs, which enhanced their compressive strength [33]. The reason was linked to the action of nanosilica as nanofiller in the lime-based binding by the precipitation of C-S-H gel, reducing thus the pore range between 20 and 100 nm and increasing the population of gel pores ($<10\text{ nm}$) [33]. Furthermore, Duran et al. [34] studied the effects of using large amounts of nanosilica (6, 10 and 20%wt with respect to lime) into air lime mortars. An increase in the water demand, a reduction in the flowability of the fresh mixtures, and a rise in the long-term strength of the air-lime mortars were detected [34].

Nonetheless, the use of nanoparticles into air lime with ceramic aggregates has not yet been studied in detail. Only in recent times, the analysis of the effect of SiO_2 and TiO_2 NPs into mortars with crushed ceramic and calcarenite sand was reported [35]. These results showed an enhancement in early compressive strength and an increased resistance against salt crystallization. Therefore, to the best of our knowledge the approach reported here is completely original.

This work aims to study the effects of the addition of Ca(OH)_2 and SiO_2 nanoparticles on the microstructural, mechanical, and physical properties of Roman ceramic-aerial lime-based mortars. The pozzolanic reactions between Roman ceramics (dust and fragments) and lime, were expected to be increased in the presence of Ca(OH)_2 and SiO_2 NPs since their small particle size and high specific surface area could rise the possibility of hydration reactions between lime binder, sand and silicon-based ceramics. Moreover, because these reactions take place in early stages [34], a special focus was placed on the effects of nanoparticles on the early age properties and workability of mortars. X-Ray Diffraction (XRD), Thermal analysis (TGA-DSC), and Environmental Scanning Electron Microscopy (ESEM) analyses were also used to discuss the effect of nanoparticles in controlling the setting, the pozzolanic activity and the carbonation reaction mechanisms of the different mortars (aerial lime based mortars blended with ceramic aggregates, and mixed with Ca(OH)_2 , SiO_2 NPs, and with the combination of both NPs). Special emphasis was also put on discussing the relationships between the pore structure and other properties including mechanical performance and capillary water absorption.

2. Materials and methods

In order to facilitate the exposure of the experimental procedure, a schematic representation of the methodology carried out is shown in Fig. 1. The detailed explanation of each experimental step is described in the following subsections.

2.1. Materials

The mortar formulation was based on a mix of silica sand and ceramic aggregates (crushed and/or finely ground bricks). A EN-196-1: 2006-compliant standardised siliceous sand (99% of SiO_2 in mass) was the aggregate used throughout. Moreover, ceramics were collected from the original bricks and tiles of the Complutum archaeological site (Alcalá de Henares, Madrid, Spain). These ceramics were grinded up to different particle size to reproduce the grain size distribution of the Roman mortars in the site [68][16] (Table 1). The chemical composition of the ceramics obtained by X-Ray Fluorescence equipment PHILIPS Magix Pro (PW-2440) was CaO 1.64%, SiO_2 53.04%, Al_2O_3 19.87%, Fe_2O_3 6.61%, MgO 7.06%, Na_2O 0.75%, K_2O 4.65%, TiO_2 0.8%, P_2O_5 0.21%, Zr 205.3 ppm and 2.54% of LOI. Finally, industrial lime putty supplied by PROIESCON S.L (Madrid, Spain), with a maturation time of four years was used as binder. According to TGA analysis, the lime putty contained 26% of CaCO_3 . Weight measurements after stove drying revealed that it had 1.3 g/cm^3 density and 20% water content.

Two types of Ca(OH)_2 NPs and one type of SiO_2 NPs were used in the study added alone and blended in combination. Specifically, three types of commercial nanoparticles were used in this research: two alcohol dispersions of nanolime at a 5g/L concentration in 2-propanol, distributed under the trade names Nanorestore® (provided by CTS, Italy), and CaLoSil® (IBZ Salzchemie GmbH & Co. Kg, Germany), which were designated in this study as NP1 and NP2, respectively; as well as Nanoestel® (provided by CTS, Italy), an aqueous colloidal solution of nanosilica (30% dry residue), which was referred to as NS. Fig. 2 shows the Transmission Electron microscopy (TEM) images (JEOL JEM 3000, operated at 300 kV) obtained for the NP1, NP2, and NS samples. The distribution and average size of the nanoparticles were determined from TEM images by a statistical analysis using the Digital Micrograph software (Gatan, Inc.), and counting at least 15 particles arbitrarily chosen in each sample. Thus, it stands out that NP1 sample exhibited hexagonal shape particles with two particle size distributions: a larger distribution around $540 \pm 132\text{ nm}$, and a smaller one around $86 \pm 12\text{ nm}$, corresponding to aggregated particles (Fig. 2a). While the NP2 sample, compared with the NP1 particles, consisted of hexagonal platelets with well-defined crystal habit and a more uniform particle size distribution of around $98 \pm 19\text{ nm}$ (Fig. 2b). Moreover, the silica sample (NS) consisted of spherical particles with a quite uniform size of around $12 \pm 2\text{ nm}$ (Fig. 2c).

2.2. Preparation of the specimens

The mortar samples were prepared with a fixed binder-to-ceramic and sand proportion by volume-ratio, equal to 1: 2: 0.5: 1 (lime: sand: ceramic dust: ceramic fragments). This ratio was also based on a preliminary research on the Roman site [16]. In addition, nanoparticle ratio was kept as 0.5:1 by volume (nanoparticle: binder) [36]. When both nano SiO_2 and nano Ca(OH)_2 were added, a relation (2):1 by volume was used, respectively, which means two volumes of SiO_2 NPs for every volume of Ca(OH)_2 NPs (Table 2). Thereby, based on the addition of the three types of nanoparticles (NP1, NP2, and NS), six types of mortars were prepared. The mixtures, with the addition of a type of nanoparticles, were named as M-NP1, M-NP2, and M-NS. Furthermore, the combination of both types of nanoparticles was called as M-NP1NS and M-NP2NS, when SiO_2 NPs (NS) was mixed with Ca(OH)_2 NPs type 1 (NP1) and Ca(OH)_2 NPs type 2 (NP2), respectively. A control mortar (M-control) without NPs was prepared as well. The constituents of the mortars and the content of each specimen are shown in Table 2.

Regarding the sample preparation and curing conditions, ceramic fragments and dust were firstly homogenized and added to the

Fig. 1. A schematic illustration of experimental methodology (Image by A. Sierra-Fernandez).

Table 1
Grain size distribution of aggregates (%).

Aggregate	Grain size distributions (%)							Total
	>2	1 < x < 2	0,5 < x < 1	0,25 < x < 0,5	0,125 < x < 0,25	0,063 < x < 0,125	< 0,063	
ceramic	30	15.43	8	16	3.61	1.78	3	77.82
sand	0	3.86	8.4	7.2	2.41	0.85	0	22.18

Fig. 2. Low magnification TEM images of the Ca(OH)₂ nanoparticles: (a) NP1 and (b) NP2; and the SiO₂ NPs: (c) NS.

Table 2
Proportion of the components used in the mortar samples (volume).

Sample	Lime putty	Ceramic dust (< 125 μm)	Ceramic fragment	Sand	Water	NP1	NP2	NS
M-Control	1	0.5	1	2	0.2			
M-NP1	1	0.5	1	2	0.2	0.5		
M-NP2	1	0.5	1	2	0.2		0.5	
M-NS	1	0.5	1	2	0.2			0.5
M-NP1NS	1	0.5	1	2	0.2	0.16		0.32
M-NP2NS	1	0.5	1	2	0.2		0.16	0.32

lime putty. The blend was mixed in a laboratory mortar mixer with helical-ribbons impeller rotated by a turbine mixer providing low speed for five minutes. This water to binder (lime water: lime putty) ratio was fixed into 0.2 volumetric ratio for all mixtures to compare the mortars having differences only in the addition of nanoparticles. Finally, the NP1, the NP2 and the NS nanoparticles, as well as their combinations (NP1NS and NP2NS) were added into the blend. Due to their high surface energy, equal diffusion of the nanoparticles in the blend is a difficult task. Therefore, proper mixing procedure was done. Dispersions of each type of nanoparticles were agitated by using a magnetic stirrer for 15 min to prevent the agglomeration of nanoparticles [20,37]. Subsequently, they were mixed with the blends for five minutes with a helical-ribbons impeller. In case of combinations, nanoSiO₂ were firstly added and mixed for five minutes then the same procedure was followed to nanoCa(OH)₂ due to its high reactivity [38]. The content of each mortar sample is shown in Table 2.

Blends were casted into 40 × 40 × 40 mm³ cubic silicon moulds into two layers and vibration-compacted. The moulds were transferred to a temperature and humidity-controlled room, where they were kept under humid conditions (>95% of relative humidity (RH) and 25 ± 3 °C) for 7 days. Specimens were demoulded after 7 days, and then were cured under controlled conditions in a ventilated chamber at 50 ± 3% RH, 25 ± 3 °C, and under a carbon dioxide (CO₂) concentration of 700 ± 103 ppm. The samples were kept in these conditions up to the tests at 90 and 120 days of curing time. In all tests, at least three samples were used for every composition, to ensure the statistical significance and reproducibility of results.

2.3. Methods

2.3.1. Flowability

The flow of the different mortars was measured as the average of the spread diameter, in mm, in a standard flow table test (EN 1015-3: 2000) [39]. The measurements were performed in all samples, before and after the addition of nanoparticles into the blends, in order to monitor the effect of nanoparticles in the consistency of lime-based mortars.

2.3.2. Macroscopic observations and weight changes

A USB-microscope (DigiMicro 2.0 Scale, dnt Drahtlose Nachrichtentechnik Entwicklungs- und Vertriebs GmbH, Dietzenbach, Germany) was used to observe the surface of the mortars immediately after demoulding. In addition, the specimens were weighed at 7, 15, 31, and 120 days of curing time to monitor the evolution of mass variations in time.

2.3.3. Mineralogical composition

The mineralogical composition of both external and internal (core, 15 mm from the surface) zones of mortar specimens was monitored at different curing times: 90 and 120 days, by X-ray diffraction (XRD), employing a Panalytical XPert MPD diffractometer and CuK α

radiation ($\lambda = 1.54 \text{ \AA}$), in Bragg-Brentano geometry. Prior to the measurements, the samples were dried in a 60 °C oven for 24 h. The measurement conditions were: 2 θ : 4–80° scan range, 2 θ = 0.03 step size, 1 sec/step time measurement, operating at 45 kV and 40 mA. Moreover, the PANalytical's X'Pert HighScore Plus v3.0 software [40] with the PDF-4 Integrated Data Analysis Software (2018 and 2019 versions) was used to identify and quantify the mineral phases. The semiquantitative analysis of the calcite/portlandite ratio was carried out using the Reference Intensity Ratio (RIR) method, recommended by the International Centre for diffraction data (ICDD) which was stated as more convenient for this kind of materials [41]. Details of this method are described in [42,43].

2.3.4. Thermogravimetric analysis

The thermogravimetric analysis (TGA) was performed to determine the carbonation level, the structural and hydration water content as well as any possible thermal decomposition of other hydraulic phases. For that, a TA Instruments SDT-Q600 thermal analyser under nitrogen atmosphere (flow rate 20 mL/min) from 20 to 900 °C with a continuous heating rate of 10 °C/min⁻¹ was employed. TA Instruments Universal Analysis DuPont 2000 was used for data processing. Analysis was conducted both after 90 and 120 days of curing on the grinded samples taken from slices 1 cm inside of each mortar sample. Prior to the measurements, the samples were dried in a 60 °C oven for 24 h.

2.3.5. Microscopic observations

Both internal and external zones of mortars fragments of 90-day-curing were analysed through an environmental scanning electron microscopy coupled with energy dispersive X-ray spectroscopy (ESEM-EDS) (FEI QUANTA 200 OXFORD INSTRUMENTS Analytical-Inca). Moreover, polarization microscopy observations were carried out on thin polished sections of the samples after 120-days curing, by using a BX51 Olympus microscopy connected to an Olympus S12 DSL camera. The Digital micrograph software was used for image interpretation.

2.3.6. Pore structure analysis

The microstructure and porosity of the different mortars were investigated with Brunauer-Emmet-Teller (BET) method (Micromeritics Tristar 3000 Analyzer). The N₂ sorption isotherms were obtained at 77.35 K under continuous adsorption conditions. High purity nitrogen gas (>99.99%) was used in all measurements. An evaluation of the pore size distribution of the mesoporous area, specifically from 1.7 to 300 nm, was carried out with the data obtained by nitrogen adsorption isotherms, and subsequent interpretation of results by means of the Barret-Joyner-Halenda (BJH) method [44]. The evaluation was carried out in the pore size distribution of micropores (~2 nm) and mesopores (2 nm < width < 50 nm) of mortars because the distribution in this range is related to the porosity of C-S-H phases and drying shrinkage [44]. This range is extremely important to assess the pore structure in lime-based matrices with pozzolanic additions and, consequently a deeper understanding of their properties.

2.3.7. Mechanical performance

The compressive strength at 120 days of curing time was performed according to the EN 1015-11:2000 [45]. The A2 kN Autotest-200/10-SW testing machine was used. Loading was applied at a constant stress rate of 0.01 N/m².s until the ultimate value was reached. The relation between the strength and the deformation was registered.

Furthermore, static modulus of elasticity was estimated by the relation between the strength and the strain at the half of the ultimate strength. In addition, both modulus of toughness and resilience were determined from the strain-stress curve. The former was calculated as the area under this curve up to the fracture point while for the latter the area up to the elastic limit was considered.

2.3.8. Bulk density

The bulk density (ρ), in kg/m³, was measured in all samples after 120 days of curing time, according to European Standard EN 1936:2007 [46]. They were determined following the Archimedes' principle (2).

$$\rho = w_d / [(w_{sat} - w_{sum}) / (\rho_{liquid})] \quad (2)$$

where w_d , w_{sat} , w_{sum} are the dry, saturated and submerged weight values of the samples, respectively; while ρ_{liquid} is the density of the liquid, in this case, distilled water at 20 °C. These results were the average of the three samples of mortars for each batch at 120 days-curing time.

2.3.9. Hydric performance

Open porosity and water absorption coefficient were determined by EN 1936:2007 [46] at 120 days of curing, using three samples for each batch. The open porosity was determined following the Eq. (3):

$$\rho = [(w_{sat} - w_d) / (w_{sat} - w_{sum})] \cdot 100 \quad (3)$$

The water absorption coefficient (C_{abs}), in percentage, was defined as the maximum amount of absorbed water that the sample could absorb (W_{sat}) compared to the dry weight (W_d), according to the Eq. (4):

$$C_{abs} = [(w_{sat} - w_d) / (w_d)] \cdot 100 \quad (4)$$

Furthermore, at 120 days of curing time, the water absorption coefficient by capillarity and sorptivity was determined by registering the weight changes of the three samples for each batch in time, in accordance with the standard EN 1015-18:2003 [47]. The samples were firstly dried in an oven (CENTERM 150 model) at 40 ± 5 °C to reach a constant mass. Then, they were introduced into distilled water in a height of 5 mm. The variation of the weight in time was registered. In addition, sorptivity at 1 min (initial rate of absorption) was calculated.

3. Results and discussion

3.1. Flowability

The consistency of the blends was determined by the flow table method. Since same water amount was added to all blends, in such a way that the flowability was mainly influenced by the NPs dispersions.

The flowability of the pastes significantly increased with the addition of nanoparticles into the blends. Therefore, before the NPs were added, flow diameters were 150 ± 5 mm and with the addition of NPs the diameters increased, ranging from 170 mm to 200 mm. This increase in flowability can be explained by the addition of nanoparticles dispersed in solvents: isopropanol in the case of $\text{Ca}(\text{OH})_2$ NPs, and water for the SiO_2 nanoparticle dispersions. Specifically, the workability increased in the following order: M-NP2 (34.4%) > M-NP1 (24.9%) > M-NP1NS (18%) > M-NS (8%) > M-NP2NS (7%). Apparently, nano $\text{Ca}(\text{OH})_2$ particles (M-NP1 and M-NP2) remarkably

increased the mortar fluidity and nano SiO_2 provoked less increase in flowability which is in accordance with previous studies [5,48] and it can be explained by the absorption of water by the SiO_2 NPs. Moreover, their strong tendency for adsorption of ionic species in the aqueous medium [49], probably caused agglomerations and packing [5]. The lowest particle size of NP2 and ability to wrap NS particles could be the reason of the differences with NP1 additions, in such a way that while M-NP2 showed the highest increase of flow diameter, the incorporation of NS particles dropped it drastically. Additionally, although the effect of solvent (isopropanol and/or water) in the mortar properties is outside the purpose of the present research, it is also important to consider that the presence of isopropanol may modify their hydration reactions and/or kinetics, because of variations in the water available for lime-based mortars hydration, with a consequent possible impact on their early age properties.

3.2. Macroscopic observations and weight changes

Results of macroscopic magnified optical polarized light microscope images are shown in Fig. 3. The comparison of images in two magnifications allows deducing the homogeneous distribution of aggregates embedded in the binder in all samples. However, it is worth mentioning that while a much rougher surface is observed for both the control mortars and mortars with nano $\text{Ca}(\text{OH})_2$ (Fig. 3a, b and c), the presence of nano SiO_2 in the mortars generated smooth and compact surfaces (Fig. 3d, e and f). This was attributed to the generation of calcium silicate hydrate (C-S-H) gel by the pozzolanic reaction between SiO_2 NPs, silicon-based ceramics and lime, which filled the voids of the lime matrix, making it more homogeneous and more compact, in agreement with previous works [1]. Moreover, the presence of lime accumulations was also particularly relevant in those mortar samples. This may be ascribed to a more intense chemical interaction between aggregates and lime, when the SiO_2 NPs are introduced into the blends as additives. Reactions rims at the interfaces between the binder and the siliceous compounds (quartz and silicon-based ceramics) were prominently detected in these samples by optical light microscopy, as will be discussed below.

Fig. 4 shows that the mass loss of mortars significantly increases with the presence of SiO_2 NPs and the combination of SiO_2 and $\text{Ca}(\text{OH})_2$ NPs, in comparison with the reference mortars. Therefore, whereas the reference samples lost their 16% of weight after 7 days of curing-time, the weight loss of mortars was around 19.8%, 21.1%, and 18.4% for M-NS, M-NP1NS, and M-NP2NS, respectively. Note that the greater weight loss kinetic was registered during the first 7 days and it was stabilised later. This could be ascribed to the changing moisture gradient between the mortar and the environment which is produced by first evaporation than the water release during the carbonation [50]. Once the equilibrium between the mortar and the environment was reached no change was recorded in weight. Only the weight of M-NS and M-NP1NS samples slightly increased after 120 days of curing. This weight gain can be due to the precipitation of hydrated forms and calcium carbonate polymorphs during the carbonation, as was confirmed by XRD and TG analysis and as will be discussed in the next sections.

3.3. Hydration and carbonation processes

3.3.1. XRD

Fig. 5 shows the XRD patterns obtained on the surface and in the core of the different mortars, after 90 and 120 days of curing. Moreover, to assess the carbonation process, the amounts of portlandite and calcite phases in the different mortars were quantified (Table 3). Overall, the XRD patterns showed peaks corresponding to the presence of quartz and hematite from aggregates as well as portlandite and

Fig. 3. Macroscopic magnified optical images of mortar samples: (a) M-control, (b) M-NP1, (c) M-NP2, (d) M-NS, (e) M-NP1NS, and (f) M-NP2NS.

Fig. 4. Weight changes detected in mortar samples after 7, 15, 31 and 120 days of curing.

calcite coming from the binder. According to the diffractograms, the carbonation process was not complete after 90 and 120 days of curing time.

In short curing periods, the comparison between the XRD profiles, performed on both the inner and outer sides indicates a common tendency marked by an increase in the content of portlandite as it deepens within the mortar, such as observed by the increase in intensity maxima. This suggests that carbonation has not yet been completed. However, it is observed that this process has achieved the nucleation of the most stable of its polymorphs; calcite (Fig. 5, Table 3) and those metastable polymorphs such as vaterite or aragonite are not identified. Additionally, no hydrated calcium carbonate phases, which are typically detected in high relative humidity environments were detected [51]. The transformation of portlandite into calcite is manifested by a higher rate on the external surface than in the internal one, as expected following the literature [52]. The diffusion of CO_2 through the pores is gradual, suggesting that the kinetics of carbonation is greater on the external surface, slowing down towards the interior [53].

At 90 days of curing, important differences were noticed in the mortar samples according to the type of nano-additives used. XRD

patterns of mortars with nano $\text{Ca}(\text{OH})_2$ revealed that M-NP1 had better carbonation than M-NP2 (Fig. 5). Previous study has shown differences in terms of crystal habit, size, aggregation level and type of atomic scale structural defects in the mentioned nano $\text{Ca}(\text{OH})_2$ colloidal solutions which favour aragonite-calcite transformation, at high relative humidity conditions (75 %RH) [54]. This could explain the different reactivity in both samples. Additionally, the XRD patterns of the mortars with SiO_2 nanoparticles (M-NS) showed greater intensity of calcite peaks than those of portlandite, both in external and internal surfaces, thus suggesting a higher carbonation rate. The fact that less portlandite was detected in the mortar samples with SiO_2 nanoparticles is also representative of the more advanced hydration process in mortars with this type of nanoparticles and silicon-based Roman brick dust. Furthermore, peaks corresponding to C-S-H phases suggest a pozzolanic activity, which is noticeable in the external part of M-NP2, M-NS and M-NP1NS after 90 days of curing, as indicated by (*) symbol and also shown in the corresponding zoom view in Fig. 5.

Although it is clear that the 120-days mortars are more carbonated, the carbonation was not yet completed since portlandite was still detected in all of them (Fig. 5 and Table 3). The external part of the mortars continued to be mainly composed of calcite because of carbonation progresses inwards. To note that the M-NP2 samples after 120 days registered a carbonation level quite similar among the core and the external surface (Table 3).

Among the nano-combinations, an increased carbonation rate was detected in M-NP2NS, as reflected in the higher content of calcite detected in both external and internal surfaces 90 and 120 days (Fig. 5 and Table 3). Peaks of pozzolanic activity products were detected in all samples after 120 days of curing. The more nano SiO_2 content had the mortar, the more pozzolanic reaction products formed. XRD peaks of these products become visible on the inner surfaces after 120 day of curing. During carbonation, silicon-based ceramic aggregate gradually released the water which was absorbed in mixing [16]. This favoured the prolonged pozzolanic reactions at 120 days of curing. Besides, small capillary pores should have led more access of CO_2 into the core of the mortar samples.

3.3.2. Thermogravimetric analysis

To better assess the pozzolanic and carbonation reaction products, thermogravimetric analysis (TGA) was performed on the mortar

Fig. 5. XRD patterns obtained on the surface and in the core of mortar samples at 90 and 120 days of curing, C: calcite, P: portlandite, Q: quartz, H: hematite, * and CSH: calcium silicate hydrate. Details of C-S-H phases are shown in the corresponding zoom view. Short-range-order (SRO) phases are highlighted in each profile.

Table 3

Relationship between calcite (C) and portlandite (P) through semi-quantitative evaluation by XRD performed on the external and internal zones of mortars.

C/P ratio	90 days		120 days	
	External surface	Internal surface	External surface	Internal surface
M-Control	74/26	34/66	57/43	41/59
M-NP1	66/34	46/54	70/30	44/56
M-NP2	62/38	46/54	79/21	83/17
M-NS	73/27	44/56	89/11	70/30
M-NP1NS	77/23	45/55	50/50	52/48
M-NP2NS	79/21	50/50	72/28	60/40

Table 4

Weight losses (%) gathered from thermal analysis (TG) data after 90 and 120 days of curing.

Sample	Time (days)	Loss 20–200 °C	Loss 350–500 °C	Loss 580–900 °C
M-Control	90	1.3	0.49	3.66
	120	0.92	0.89	4.07
M-NP1	90	0.95	0.58	3.76
	120	0.79	0.74	4.36
M-NP2	90	0.77	0.65	3.57
	120	0.68	0.86	3.72
M-NS	90	1.43	0.76	3.57
	120	1.55	1.08	3.57
M-NP1NS	90	3.21	0.41	2.85
	120	1.16	0.8	3.91
M-NP2NS	90	1.14	0.6	2.92
	120	1.53	0.82	3.81

samples. Table 4 presents the weight losses and Fig. 6 shows the rate of weight loss against temperature (DTG curves) after 90 and 120 days of curing. Each exothermic peak in the curves is associated with the weight loss of certain phases: i) below 200 °C is associated with the moisture in the mortar and C-S-H dehydrate; ii) temperature range 350–500 °C is associated with the dehydration of $\text{Ca}(\text{OH})_2$ and C-S-H; and iii) the decomposition of CaCO_3 occurs between 580–900 °C, associated with CaCO_3 decomposition [52]. However, the interpretation of thermal analysis in the mortar mixes can be more complex because of the different thermal stability of nanocrystals [55]. The other important point to be emphasized is that metastable calcium carbonate polymorphs and hydrated amorphous calcium carbonate are decomposed in the same temperature region (400–600 °C), may thus result in an overlap of peaks [56].

As expected, more weight loss occurred in the range which is attributable to the decomposition of calcite and the peak increased at 120 days. This suggests a greater carbonation degree after 120 days of curing time, which agrees with XRD results. Moreover, noticeable

differences in the degree of pozzolanic reactions could be established in the samples with nanoSiO₂ (Fig. 6 and Table 4). Nanosilica acts as a nucleation point to promote hydration reactions [57]. Overall, those reactions were promoted at early ages since the values decreased at 120 days, except M-NS and M-NSNP2 samples. This can be explained with the retardation effect of the flocculated nanosilica which filled the pores between the lime particles. Less pozzolanic reactions occurred in the samples with nanoCa(OH)₂ than control sample. This means, although in all samples the pozzolanic reactions are favoured by the moisture absorbance capacity of the silicon-based ceramics, excess Ca/Si ratio in these samples hindered the further reactions promoted by nanoSiO₂. These findings confirm the XRD results. In addition, the lower pozzolanic activity detected in the case of the mixes could be associated with the presence of isopropanol which can remarkably delay and suppress the hydration reactions [57].

Fig. 6. DTG curves of mortar samples at 90 and 120 days of curing.

Meanwhile, the carbonation reaction was delayed in the mortar samples with nanoSiO₂ additions after 90 and 120 days of curing. After 120 days of curing, carbonation reaction rate of the M-NS, the M-NP2NS, and the M-NP1NS samples decreased by 12.28%, 6.38%, and 3.93%, respectively (Table 4). Because pozzolanic reaction dominated carbonation reaction as a result of the competition between them and less lime was left to carbonate [58]. When the lime is consumed in the pozzolanic reaction the unreacted silica starts to react with the C-S-H and the ratio of Ca/Si falls [58,59]. Furthermore, DTG curves of the M-NP1NS and the M-NP2NS samples showed peaks around 750 °C and 980 °C after 120 days of curing (Fig. 6), which may imply phenomena of re-carbonation [7]. This is in line with our previous study [16], in which was revealed that the use of ceramic in lime-based mortars induced re-precipitation phenomena, due to the increased solubility produced by ceramic dust and non-stable pozzolanic activity products. Besides, the higher mass loss associated with the CaCO₃ was registered in the M-NP1 samples, in comparison with the M-Control mortar, after 120 days of curing, suggesting a higher degree of carbonation in these samples. This content of carbonates was different to that obtained by XRD analysis because the sample fragments analysed by TGA was an average sample, combining material from the surface of the mortar with material from the core, whereas XRD analysis was carried out in both external and internal surfaces of mortars.

After 120 days of curing, the weight losses registered between the temperature ranges ca. 350–500 °C did not reduced but incremented

for the M-NP2 samples (Fig. 5). Furthermore, the most significant increase was detected in the M-NP1NS and the M-Control, followed by the M-NS and the M-NP2NS samples (Table 4). As it was mentioned before, this temperature range is associated with the dehydration of portlandite; however, this relevant increase could also be attributed to the decalcification of the detected C-S-H phases, which were less stable. It has been observed in lime-pozzolana mortars that first hydration reaction occurs, whereas the carbonation reaction prevails afterwards by attacking not only lime but also the hydrated phases leading to their decalcification [58,59]. This ion leaching process is dependent on the level solubility of the medium. The greater the Ca/Si ratio of the C-S-H the higher the solubility [60]. On the other hand, metastable calcium carbonates of low thermal stability also decompose in this temperature range [56]. Thereby these peaks could be also attributed to the presence of carbonate polymorphs and hydrated amorphous calcium carbonate, as mentioned above. Likewise, broad humps observed in the transient zone between 500 °C and 650 °C in the M-NS, the M-NP1NS and the M-NP2NS samples (Fig. 6) may be associated with amorphous carbonated phases [61].

Additionally, the rate of hydraulicity of the mortars was examined. Thus, Fig. 7a presents the correlation between carbon dioxide, released from the mass losses during the decomposition of samples, and its ratio with structurally bound water related to hydraulic compounds, and Fig. 7b shows the ratio of CO₂ versus chemically bound water. These ratios inversely express the hydraulic character of the mortars. Based on these findings, the mortars showed a highly hydraulic nature,

Fig. 7. Plots showing the correlation between (a) CO₂/H₂O and CO₂, (b) H₂O and CO₂ at 90 and 120 days of curing.

since the $\text{CO}_2/\text{H}_2\text{O}$ ratio was below 10 and close to the connection of axes [35] (Fig. 7a). Apparently, the hydraulic nature of mortar samples developed at 120 days was quite different than the theoretical trend which would be above the values of 90 days (Fig. 7a). This could be due to the high percentages of structurally-bound water belonging to C-S-H and clay minerals from Roman bricks in the mortars (Fig. 7b). Thereby, in their decomposition the partial or full release of calcium ions from C-S-Hs to pore water and silicic acid and calcium hydrate increased.

3.4. Assessment of the micro and mesoporous structure

A comparative ESEM microtextural analysis was carried out in the mortar samples, at 90 days of curing time. Compared to the control (Fig. 8a), the mortars modified by $\text{Ca}(\text{OH})_2$ NPs showed similar texture and morphology (Fig. 8b and 8c). Similar pores and micro cracks filled with many micrometric secondary CaCO_3 crystals were observed in the M-NP1 and the M-NP2 samples (Fig. 8b and c, inset, respectively). After 90 days of curing, because of produced C-S-Hs an increased

compaction of the binding matrix with a low surface roughness was registered in the M-NS, M-NP1NS, and M-NP2NS samples (Fig. 8d, e, and f). Nanosilica addition also resulted in the generation of various microcracks which could be attributed to the drying and carbonation shrinkage (Fig. 8g and h).

As can be seen in Fig. 9, thin sections observations under polarized optical light microscopy highlighted the reactions rims at the aggregate-binder interfaces, at 120 days of curing in both M-Control and M-NS mortars (Fig. 9a-c, and Fig. 9b-c, respectively). The lime binder, $\text{Ca}(\text{OH})_2$, generates an alkaline environment that favors a physicochemical reaction between the matrix and the siliceous compounds (quartz and silicon-based ceramics) producing a rim at the edges of these compounds [14]. In this way, when nano SiO_2 additions are used, the solubility of the binder increased leading to dissolution and re-precipitation of new phases, which can be found filling those cracks generated by the retraction and dissolution of the binder, as can be seen at the edges of aggregates of the M-NS sample (Fig. 9 b and d).

In M-control sample the boundary reaction products were evidenced around ceramic aggregate and quartz grain (Fig. 9a and c), whereas in the M-NS sample the reaction rims were prominently observed (Fig. 9

Fig. 8. ESEM images of mortar samples at 90 days of curing, and the optical line-scan profiles (below) obtained after processing of micrographs by Digital Micrograph software: (a) M-control, (b) M-NP1, (c) M-NP2, (d) M-NS, (e) M-NP1NS, and (f) M-NP2NS. To note the generation of microcracks detected on the surface of the specimens M-Control and M-NS (g and h, respectively).

Fig. 9. Thin section images of mortar samples at 120 days of curing: (a-c) M-Control; and (b-d) M-NS. Reaction rims around the ceramic grains are marked.

b and d). The EDS spectra (not shown) of these samples revealed an aluminium and silicon enrichment in the brick-binder interface, as a result of the hydraulic reaction between both components. Thus, the rims in the M-NS samples are dispersed along the matrix, filling the pores and/or discontinuities of its structure. This phenomenon can be shown in the framed area of these samples (Fig. 9b).

Modification of the micro and mesopore structure (BJH curves and N_2 adsorption/desorption isotherms) for the different samples is shown in Fig. 10, while Table 5 summarizes the BET results (BET-surface area, pore volume and pore size) of mortars unmodified and modified with nanoparticles.

Differences in pore size distribution (Fig. 10) indicated that M-NS, M-NP1NS, and M-NP2NS samples showed a larger volume of pores in comparison with the control and samples with $Ca(OH)_2$ NPs. Thereby, a higher total pore volume was detected in the following order: M-NS ($0.036 \text{ cm}^3/\text{g}$) > M-NP1NS ($0.035 \text{ cm}^3/\text{g}$) > M-NP2NS ($0.034 \text{ cm}^3/\text{g}$) > M-Control ($0.022 \text{ cm}^3/\text{g}$) > M-NP1 ($0.019 \text{ cm}^3/\text{g}$) > M-NP2 ($0.018 \text{ cm}^3/\text{g}$) (Table 5). Remarkably, the average

Table 5

Specific surface area (S_{BET}), total pore volume and average pore size of the different mortar samples at 120 days of curing.

Sample	S_{BET} (m^2/g)	Pore Volume (cm^3/g)	Pore Diameter (nm)
BJH Adsorption			
M-Control	3.66 ± 0.24	0.0219	23.59
M-NP1	3.26 ± 0.03	0.0187	21.59
M-NP2	3.18 ± 0.02	0.0185	23.24
M-NS	7.23 ± 0.05	0.0364	20.06
M-NP1NS	5.72 ± 0.04	0.0353	26.21
M-NP2NS	5.61 ± 0.03	0.0341	23.55

volume around 40 nm (mesopore range) increased from 0.26 in M-control to 0.41, 0.43, and $0.48 \text{ mm}^3/\text{g}$, in M-NP2NS, M-NP1NS, and M-NS samples, respectively (Fig. 10). This increase is attributed to the shrinkage cracks, related to the volumetric changes of mortars during the drying and curing periods and consistent with the results obtained by ESEM analysis. Wang et al [57] have showed how the use of isopropanol to replace a part of mixing water in cementitious materials can heavily impact on its drying, generating shrinkage cracks. Moreover, a larger volume of gel pores ($<10 \text{ nm}$) was detected for the M-NS samples, as Fig. 10 shows. The higher total pore volume detected in these samples with SiO_2 NPs could be ascribed to the formation of C-S-Hs, as was detected by XRD and TG analysis, because a greater number of pozzolanic reactions occurred between Ca^{2+} ions (from lime and NPs) and Al^{3+} , Si^{4+} ions (from the aggregates and NPs). The increase in mesopores can also be attributed to the shrinkage induced microcracks which were detected by microscopy (Fig. 8 g and h). This microcracking is typically produced in connection with the dehydration and polymerization of the hydrous silica products [62]. A higher capillary stress due to the water meniscus is developed in the mesopores volume of mortars, leading to a greater drying shrinkage [63]. Moreover, the high surface area of nano SiO_2 typically consumes a high amount of water resulting thus in an increased shrinkage [62]. On the contrary, $Ca(OH)_2$ NPs generated a slight decrease in the pore volume, 15.6% for the M-

Fig. 10. BJH pore-distribution curves of mortar samples at 120 days of curing.

NP2 sample and 14.5% for the M-NP1 sample (Fig. 10). This could be a result of pore blocking during the carbonation of the mortars with nanoCa(OH)₂. As was shown by microscopy (Fig. 9), cracking porosity in the binder has been undergoing self-healing in these mortars due to the re-precipitation of CaCO₃, in agreement with other studies [16].

On the other hand, the measurements of BET-surface area showed that the incorporation of nanosilica induced greater values in lime-based mortars (Table 5). Therefore, this parameter rises from 3.66 m² g⁻¹ for the control sample to 5.61 m² g⁻¹, 5.72 m² g⁻¹, and 7.23 m² g⁻¹, for the M-NP1NS, M-NP2NS, and M-NS samples, respectively. This increased surface area was related to the new gel pores produced by the carbonation of C-S-H phases and the microcracking generated during drying and carbonation [62].

3.5. Mechanical performances

In Fig. 11 the compressive strength of the different mortars at 120 days of curing time is shown. As can be seen, the addition of nanoparticles provoked a sharply decrease of the strength (Fig. 11). The greatest decrease in strength was seen in M-NP1 and M-NP1NS mortars samples up to 72% and 68%, respectively. Furthermore, comparing M-NP1 and M-NP2, the highest homogeneous carbonation detected in the M-NP2 samples can justify differences among them.

In all the cases, this fall in the compressive strength detected in the mortars modified with nanoparticles can be explained considering different factors: i) the relevant increase in flowability detected in samples with nanoparticles due to the difference of water:binder ratio; ii) the higher shrinkage effect provoked by the use of isopropanol as aforementioned and; iii) the non-homogeneous distribution of

carbonation depth detected in these samples, which was marked by the generation of a superficial harden carbonated layer, making more difficult the CO₂ diffusion.

Since SiO₂ NPs could tend to agglomerate at early ages, the degree of pozzolanic products at 120 days led to a medium compressive strength. Furthermore, this overall loss of mechanical properties can be also attributed to the resulting decalcification of highly polymerized C-S-H phases. These phases are unstable and probably decomposed by carbonation. Cizer et al. [58] have also reported that the use of highly reactive pozzolanic materials in lime mortars may not provide enough strength development in these materials due to the phase modification. Moreover, the shrinkage microcracks detected in the samples with SiO₂ NPs additions (Fig. 8g and 8h), could also weaken the interface between compounds with the consequent strength reduction.

The displacement-stress curves of mortar samples showed that nanoparticles decreased the modulus of elasticity compared to the control samples (Fig. 12), in agreement with other studies [20]. However, the lowest stiffness detected in samples with NPs solutions compared to the reference mortars was not in agreement with Nunes et al. [1]. These authors found that SiO₂ NPs generated a higher stiffness in mortars as a consequence of the matrix densification. Once again, this discrepancy can be mainly explained by the water/binder ratio modification, the loss of densification of the matrix as well as differences regarding the type of SiO₂ NPs used (e.g. particle size, shape, chemistry and/or textural properties). Moreover, the kinetics of carbonation, which was appeared to be not homogeneous in mortar samples (Fig. 5), depends on local physico-chemical reactions. Consequently, carbonate and C-S-H phases can be aleatory crystallized in the mortar depending on the ion concentration and the environmental conditions. XRD results which are in agreement with TGA, showed how the presence of SiO₂ NPs promoted further pozzolanic reactions with a lower carbonation degree (Fig. 5, Fig. 6). The pressure may be locally concentrated at the contacts between aggregates, binder and NPs creating stress points, favouring, eventually, different damage degrees. Thereby, this could be reflected in the mechanical properties. Moreover, it should be noted that the results showed an increased plastic performance in all mortars with nanoparticles (Fig. 12). The use of nanoparticle solutions as additives thus enhanced the deformability capacity of mortars. These findings are of great interest for the application of these materials as restoration mortars since guarantee their compatibility with the existing building materials [7].

Otherwise, Fig. 13 shows the changes in modulus of toughness and resilience values of the specimens. These results showed the same trend as the compressive strength in such a way that the highest values were achieved by the control mortars, whereas the lowest values

Fig. 11. Uniaxial compressive strength values of mortar samples at 120 days of curing.

Fig. 12. Modulus elasticity values of mortar samples at 120 days of curing.

Fig. 13. (a) Toughness and (b) resilience values of mortar samples after 120 days of curing.

were reached by M-NP1 and M-NP1NS samples (Fig. 13a). These results imply that differences in terms of carbonation advance in these mortars had higher influence on toughness than pozzolanic activity products (Fig. 5).

On the other hand, among mortar samples with NPs, individual use of SiO₂ NPs caused a higher modulus of toughness and resilience and larger static deformation than samples without them (Fig. 13a and b, respectively). These results are in agreement with XRD analysis (Fig. 5) in the sense that higher carbonation and hydrated products were detected in both surfaces of M-NS at 120 days. Different from their compressive strength performance, the modulus of resilience of the M-NP2 samples increased to same value as the M-NP2NS samples (Fig. 13b). These results imply that the high internal pozzolanic activity products provided more deformation capacity to the M-NP2 mortars. On the other hand, the lack of internal CSH and more heterogeneous carbonation previously detected by XRD in the M-NP1 mortars (Fig. 5) could be the reason for its less resilience, in comparison with the M-NP1NS samples (Fig. 13b). These outcomes stated that the presence of CSH implied high rates of strength which are enhanced in combination with a high ratio of carbonation. Finally, it should be highlighted that a high deformation capacity of the samples with SiO₂ NPs in the elastic portion could enhance the earthquake resistance as stated by different authors [7,64,65].

3.6. Hydric performance

The physical and hydric performance of the different mortar samples are listed in Table 6. As can be seen, adding the solutions of both Ca(OH)₂ and SiO₂ nanoparticles reduced the bulk density of lime-based mortars (Table 6). Whereas the bulk density of the control samples was in accordance with the literature [14], the addition of SiO₂ NPs induced the greater decrease in bulk density (Table 6). Specifically,

Table 6
Bulk density, open porosity and water absorption coefficient of mortar samples at 120 days of curing.

Sample	Bulk density (kg/m ³)	Open porosity (%)	Water absorption coefficient (%)
M-Control	1663.94 ± 1.38	31.82 ± 0.03	19.12 ± 0.00
M-NP1	1585.43 ± 2.41	34.62 ± 0.02	21.84 ± 0.04
M-NP2	1595.59 ± 4.41	34.36 ± 0.11	21.53 ± 0.13
M-NS	1489.37 ± 3.30	36.58 ± 0.34	24.56 ± 0.28
M-NP1NS	1476.85 ± 3.48	40.39 ± 0.18	27.35 ± 0.18
M-NP2NS	1507.10 ± 0.00	38.61 ± 0.00	25.62 ± 0.00

the largest decrease was observed in the M-NP1NS samples (up to ~11.2%), followed by the M-NS mortars (~10.5%) and M-NP2NS (~9.4%). To a lesser degree, mortars with nano Ca(OH)₂ showed a reduction of about 4%–5% compared to the control (Table 6). In all the cases, the increase in water/binder ratio obtained by the addition of nanoparticles solutions to the blends justified this performance [64,66].

Conversely, changes in the open porosity followed the opposite trend than bulk density (Table 6). Therefore, after the curing period of 120 days, compared to M-control the open porosity increased by ~9% and ~8% in the M-NP1 and the M-NP2 mixes, respectively (Table 6). This was attributed to the presence of pores and micro-cracks filled by precipitated calcium carbonate in these samples, as was previously showed by ESEM analysis (Fig. 8b and 8c). Most remarkably, the addition of SiO₂ NPs, and its combination with Ca(OH)₂ NPs induced an increased open porosity compared to the control samples, of around 15%, 17%, and 21% for the M-NS, the M-NP1NS, and the M-NP2NS, respectively (Table 6). The consequent changes in the mortar mineralogy and microporous network, together with a larger amount of gel pores due to the formation of C-S-H phases, explain such increase in open porosity. Furthermore, the modification in water/binder ratio and the shrinkage microcracking can also contribute to induce higher open porosity.

Water absorption coefficient followed the same performance than open porosity (Table 6). Therefore, whereas an increase in the range of 12–14% can be observed when Ca(OH)₂ NPs were added to mortars; an increase from 28% in the M-NS samples, to 34% and 43% in the M-NP1NS and the M-NP2NS samples, respectively, was obtained. Overall, porous structures with larger surface areas are beneficial for absorption processes due to the higher contact area between compounds [67]. Consequently, the larger specific surface area induced by SiO₂ NPs in mortars (Table 5) lead to significant increase in water absorption coefficient in comparison with control mortars.

Moreover, Fig. 14 shows the variation of water absorption by capillarity with the times square root for the different mortar mixes. All samples were saturated at 10 min, which revealed the high volume of capillarity pores in the samples. The coefficient 10–90 was almost null in the case of the mixes with nanoparticles and 0.06 kg/m².min⁻¹ in the control one. As was expected, while mortars with nanoCa(OH)₂ showed values almost similar to the control ones, the highest rate of absorption by capillarity was achieved with the presence of nanoSiO₂ in samples (Fig. 14). Once again, it was attributed to the increase in the surface area of these samples. Moreover, the addition of NPs dispersed in solvents (isopropanol and water) could generate small sorption pores (<0.1 μm) in the binder, inducing C-S-H dissolution. It is also worth mentioning that at 90 min M-NS samples showed swelling and dry external layer (not shown). This non-homogeneous water retention

Fig. 14. Water absorption through capillarity of mortar samples after 120 days of curing.

is probably related to the flocculation and depletion forces of the SiO_2 NPs which caused lime lumps at early ages (Fig. 3). Filling effect of nanoparticles additions in mortars and the reduction in the mean pore size could also explain such performance, in agreement with other studies [1,5].

4. Conclusions

This study investigated the influence of Ca(OH)_2 and SiO_2 nanoparticles on the microstructure, the mechanical performance and the physical properties of air lime mortars with Roman ceramics. The effect of nanoparticles in controlling the pozzolanic activity and the carbonation process of the lime-ceramic mortars was also deeply studied. The main conclusions are summarised as follows.

- 1- In fresh state, results indicated that flowability significantly increased when the nanoparticles were added in the pastes, because of their dispersion in solvents. Mortars with nanoCa(OH)_2 showed the largest increase compared to the others, contrary to the nanoSiO_2 particles addition due to the agglomeration and packing trend of the latter's.
- 2- Regarding the effect of nanoparticles in the mineralogy of air-lime ceramic mortars:
 - In general terms, the mortar samples showed a highly hydraulic nature. Among the nanoCa(OH)_2 additions, the type 1 (NP1) induced an improved carbonation reaction compared to that of the type 2 (NP2), at 90 days of curing. However, after 120 days of curing, the latter showed higher carbonation degree, resulting in a more gradual carbonation rate. The rapid clogging of pores in the samples with NP1, suppressed the CO_2 diffusion from the surface to the interior of samples. This slowed down the carbonation advance. Moreover, less pozzolanic reactions were detected in these mortars. Pozzolanic activity is directly related to stoichiometric ratio of Ca/Si in the blends. The excess of that ratio and the presence of isopropanol in these samples delayed the hydration reactions, thus lowered the pozzolanic activity.
 - Adding nanoSiO_2 allowed a substantial increase in the hydraulic properties of the mortar samples, since more hydrated phases were formed in them. Interestingly, a more progressive carbonation degree was also found in mortars with the addition of nanoSiO_2 . Reaction kinetics was more dynamic in those mortars. The carbonation reaction occurred not only with lime but also with the C-S-H phases, thus allowing their decalcification with the consequent generation of gel pores ($< 0.1 \mu\text{m}$).

- 3- Concerning the effect of the nanoparticles on the mortar's microstructure and hydric performance:
 - Overall, the presence of nanoparticles lowered the bulk density and increased the open porosity in air lime-ceramic mortars. Adding them dispersed in solvents caused changes in water/binder ratio and eventually in mortars' mineralogy and pore structure. During hardening microcracks were generated.
 - Filling of microcracks with precipitated CaCO_3 were detected in samples with nanoCa(OH)_2 solutions, which caused a decrease in the pore volume and consequently less water intake by capillary absorption similar to control samples.
 - The addition of nanoSiO_2 and the combined use of nanoparticles (SiO_2 and Ca(OH)_2) provoked more compact and less rough surface. These mortars exhibited also the highest surface area and pore volume with a larger amount of gel pores ($< 10 \text{ nm}$). Shrinkage caused the union of these pores forming microcracks on the surface of the mortars. Filling of these microcracks also occurred in these mortars; however, not only with secondary calcium carbonates but also hydrated phases. Due to the less stability of the newly precipitated phases the subsequent dissolution happened. Therefore, first combined use of NPs, then only nanoSiO_2 addition increased remarkably the capillary action.

- 4- Regarding the mechanical performance:
 - A detrimental strength development was detected in mortars with nanoparticles, which was ascribed to the poor stability of the hydrated phases generated and/or the presence of microcracks in these mortars.
 - Among NPs additions, nanoSiO_2 alone and combined with nanoCa(OH)_2 induced higher toughness and resilience when more homogeneous carbonation and hydration reactions occur, respectively. This less resistance to microcrack propagation and both plastic and elastic deformation capacity of the mortars with NPs could enhance their compatibility with existing adjacent building materials in archaeological sites.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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