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Edited by José Ignacio Álvarez, José María Fernández,
Íñigo Navarro, Adrián Durán, Rafael Sirera

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Lime-based rendering mortars with photocatalytic and hydrophobic agents: assessment of the water repellency and biocide effect

Jesús Fidel González-Sánchez[1], Burcu Taşçı[2], Guillermo Martínez de Tejada[3], José M. Fernández[1], Íñigo Navarro-Blasco[1], José Ignacio Alvarez[1]

(1) MIMED Research Group, Chemistry Department, University of Navarra, mimed@unav.es, jgonzalez.65@alumni.unav.es, jmfdez@unav.es, inavarro@unav.es, jalvarez@unav.es

(2) Department of Architecture, Izmir Katip Çelebi University, burcutasci@iyte.edu.tr

(3) Microbiology and Parasitology Department, School of Medicine, University of Navarra, gmartinez@unav.es

Summary

Different rendering mortars were prepared by mixing air lime and air lime-pozzolanic nanosilica with TiO_2 and sodium oleate as, respectively, photocatalytic and water repellent agents, added in bulk. The aim of the work was to design and obtain new rendering mortars with improved durability focusing in the reduction of the water absorption of these materials and in their self-cleaning and biocide effect. To achieve a better distribution of the TiO_2 particles, which was expected to enhance their efficiency, different dispersing agents were also incorporated to the fresh mixtures. Four diverse polycarboxylate ethers superplasticizers and a poly-naphthalene-sulfonate were tested. Workability and fluidity of the fresh rendering mortars were determined to guarantee the applicability of the final products. Water contact angle was monitored with the aim of assessing the hydrophobicity of the mortars lent by the water repeller. The biocide effect was studied by means of the culture of a strain of *Pseudomonas fluorescens*. The colonization of the mortars' surface was analyzed by determining the number of colonies forming units (CFU) after several days subjecting the samples to suitable T and RH conditions. At the same time, the surface of the mortars was irradiated with solar light to activate the photocatalyst. Results showed the efficiency of the sodium oleate in reducing the water uptake of the rendering mortars. Good compatibility between the water repellent agent, the pozzolanic additive and some of the polycarboxylate superplasticizers was observed. The presence of the photocatalyst was found to be very effective in preventing microbiological colonization.

Keywords: Lime Superplasticizers; Titania; Biocide

Introduction

Scientists are nowadays facing major challenges in air pollution. One remaining challenge is to study ways of decomposing dirt caused by the organic species deposited on the building surfaces, which are responsible for the deterioration of building materials.

It should be noted that the deposition of atmospheric particles, aerosols or even the irreversible formation of black crusts - deposits of carbon particles, often sulphated - and, in general, deposits of hydrocarbon compounds, as well as the appearance of biological colonization, cause aesthetic problems to the historic building. It is also a way to initiate irreversible alterations in building materials especially stone and mortar [2]

In addition, the presence of these deposits causes high maintenance costs, eliminating them through laser ablation processes or sandblasting, which can be harmful for the historic material [3].

Photocatalysts incorporated to historic building materials can be an interesting solution to provide lower maintenance and cleaning costs by reducing surface soiling destroying organic products through a photocatalytic oxidation reaction [1]. There are different photocatalyst additives of great importance. Among them, TiO_2 stands out clearly. These additives, usually semiconductors based on oxides of the transition elements, through the action of light (for TiO_2 in the ultraviolet spectrum, UV), allow the chemical decomposition / oxidation of pollutants and deposits of organic matter [4]. In addition, these additives show biocidal efficiency by avoiding biological colonization on mortars such as algae, lichens or cyanobacteria [5]. Photocatalysts break the bonds between microorganisms and substrates (stone or mortar).

The TiO_2 photocatalysts have been investigated extensively for the killing or growth inhibition of bacteria [5-7]. Most works have been done by using a fine TiO_2 powder and a strong UV light. A little work has been reported in the use of TiO_2 nanoparticle aqueous solutions coated on substrates [8,9]. Recently, nanosized (<100 nm) TiO_2 particles have attracted a lot of activity from many researchers [10]. These nanometer-sized TiO_2 particles exhibit many special properties due to the fact that the small TiO_2 particles offer a very large surface area.

One of the drawbacks of these photocatalysts is related to the photo-induced superhydrophilicity, which could lead to the formation of water film on the surface of the renders. The uptake of water would result in severe decay processes. The addition of a water repellent agent is aimed to minimize this problem. Furthermore, in order to synergistically improve the self-cleaning and biocidal activity of the new lime-based renders, the water repellent is also expected to hinder the anchorage of microorganisms and dirt due to the superficial hydrophobicity.

In the current research work, nano-particles of photocatalytic additives (titania) in bulk were applied. Different samples were prepared with diverse superplasticizers, SPs. The use of different polycarboxylate-based superplasticizers (PCE1, PNS, 52IPEG, 23APEG and 45PC6) prevented nano-particles from agglomeration. These SPs were added to optimize the distribution of the photocatalysts improving the remotion of dirt and biological deposits. Also, water repellents were used to minimize water entry ways to lime-based mortars.

The as-obtained lime-based rendering mortars could be useful for the preservation of the Built Heritage as materials with self-cleaning and biocidal capacities. They will help to significantly reduce the maintenance and cleaning costs by preventing damage of the use of chemicals or abrasive agents in restoration works.

Materials and methods

Preparation of the mortar.

The weight proportions of the mortars were: 25% slaked calcitic lime supplied by Cal Industrial S.A. (Calinsa Navarra), classified as CL-90 by European regulations; 75% calcareous sand (Class AF-T -0/1-C sand, supplied by HORPASA Group). In addition, when necessary, the following components were added with respect to lime: 20% mineral pozzolan (nanosilica, supplied by ULMEN Europa); 0.5% water repellent agent (sodium oleate, provided by ADI-CENTER); 2.5% of nano-particles of bare TiO_2 (Aeroxide P25, Evonik) as photocatalyst; 0.5% or 1.0% of five superplasticizers were also used: three different polycarboxylate-based polymers (52IPEG is based on the copolymerization via free radical from acrylic acid and isoprenyl ω-hydroxy polyethylene glycol macromonomers; 23APEG contains α-allyl-ω-methoxy poly(ethylene glycol) macromonomers containing 23 ethylene oxide units and an equimolar amount of maleic anhydride; 45PC6 is composed of methacrylic acid and the macromonomer ω-methoxy poly(ethylene glycol) methacrylate ester with 45 ethylene oxide units at a molar ratio of 6:1) these SPs have been used and characterized in a previous work [14]. Additionally, two commercial superplasticizers (PCE1, Melflux's BASF commercial product PNS, Melcret® 500F, BASF Construction Polymers, Trostberg/Germany,) were also employed.

The mixing water was fixed at 28%, resulting from an adjustment of the water demand of the control mortar (additives/admixtures-free) to obtain a slump of ca. 160 mm as measured in the flow table test.

For the preparation of the pastes, lime and the required amount of calcitic sand (limestone aggregate) were blended for 5 min using a solid-admixtures mixer BL-8-CA (Lleal, S.A., Spain). Afterwards, the necessary water and superplasticizers were then added and mixed for 90 s at low speed and adjusted according to UNE-EN 196-1 [13], in a Proeti ETI 26.0072 (Proeti, Madrid, Spain) mixer.

Afterwards, mortars were cast in cylindrical moulds (36 mm height and 40 mm diameter) and demoulded 7 days later, stored at 20 °C and 60% RH. Different curing times were considered: 28 and 91 days. In order to make the results representative, three replicates of the mortars were tested at each curing time. Afterwards the samples were cut into three discs to have replicates during the test.

Fresh-state tests

The tests of the mortars at plastic state started with the slump measurements, which were recorded after 15 strokes of the flow table, 1 per second according to the indications of the standard UNE-EN 1015-3.

Then the period of workability of the material was determined according to standard UNE-EN 1015-9. Every 15 minutes a probe was slowly introduced, monitoring the weight until this weight was higher than 1500 g.

All these experiments were carried out by triplicate and the depicted values are an average value of all the recorded measurements.

Hardened-state tests

The mechanical resistances were measured at 28 and 91 days, to observe possible modifications over time. For all these measurements, 3 specimens were tested, in order to obtain representative values. For the compressive strength tests, a compression breaking device Proeti ETI 26.0052 was used at a breaking speed 5-50 KP $\cdot$ s^{-1} with a time interval between 30 and 90 seconds.

Hydrophobicity: water contact angle

The evaluation of the hydrophobicity of the sample was carried out with a measuring instrument of the contact angle OCA 15EC Dataphysics. In this way it was possible to determine the contact angle of a drop of water deposited on the surface of the sample, and the time for the absorption of the same by the material.

Photocatalytic activity: NO abatement

Photocatalytic activity was studied in a flow-through experiment that has been adapted from an ISO standard method [13]. In this experiment the photocatalytic oxidation of nitric oxide was continuously monitored and used as an indicator of the photocatalytic activity. Experimental conditions were 50 ± 10% RH and 25 ± 2 °C. The cylindrical photoreactor (height 12 cm; diameter 14 cm) was fed by a 500 ppb NO stream. Concentrations of NO and NO_2 were determined by a chemiluminescence detector (Environment AC32M) at a 0.78 $L\cdot min^{-1}$ flow. Experiments were carried out for discs of the samples prepared as above explained (height 1 cm; diameter 4 cm). The total exposed area of the discs was 25.14 cm^2. UV illumination (Osram Ultravitalux 300 W) was irradiated.

Biocidal study

To develop this experiment, an environmental strain of Pseudomonas fluorescens was used. Fresh cultures were obtained from stocks at -80ºC stored in 10% skimmed milk and propagated on plates of Luria Bertani culture medium (LB-agar). Bacterial growth in liquid medium was performed in LB broth in an oven at 37°C and with orbital shaking (180 rpm). To prepare the bacterial inoculum, fresh cells were first obtained on an LB-agar plate grown for 18 hours. With these cells, a suspension was prepared which was adjusted with sterile saline solution (0.9% NaCl in distilled water) to an optical density of 0.04 to 600 nm, equivalent to 5 x 10 EXP 7 colony forming units (CFU) / mL, approximately. On the day of the experiment, the cylinders were hydrated for 2 hours in LB and then each cylinder was inoculated on its upper surface with 200 μL (microliters) of the suspension, equivalent to 1 X 10 EXP 6 CFU / mL (i.e., one million CFU), approximately. After incubation in the chamber for 5 days at 37°C, the upper surface of the cylinders was scraped homogeneously with a sterile spatula and the material was resuspended in 1 mL of sterile saline. The amount of material peeled off the cylinders (mg) was determined by weighing the tube before and after placing the material from the cylinder therein. After vigorously homogenizing this suspension in a mechanical agitator, the number of bacteria present in the suspension was determined by viable count. For this, successive dilutions of the suspension were made in tubes containing sterile saline and 50 μL were transferred to LB-agar plates which were incubated at 37°C for 48 hours.

Results and discussion

Fluidity and workability (open time)

The fluidity was studied for every mixture, with and without the presence of superplasticizer. Figure 1 shows how the fluidity of the lime grouts is affected after mixing with a water-repellent agent and with a pozzolan, both causing a fluidity reduction. As it can be seen the L-O mixture showed a lower fluidity than that of the plain lime mortar, and the presence of the pozzolanic addition (nanosilica) also resulted in a sharper fluidity decrease. In the mixture L-O after the addition of 23 APEG and 45 PC6 at 1.0% the fluidity of the mixture dramatically increased, exceeding the value of 300 mm, resulting in a high-fluidity mixture. In the mixtures with other SPs at any dosage the behaviour was very similar between them.

The workability of the different mixtures is depicted in Figure 2. Compared with plain lime mortars, the addition of the sodium oleate accelerated the setting time of the sample, while – unexpectedly- the addition of the pozzolanic agent delayed it.

The workability suffered substantial changes when the SPs were added to the mortars. The setting time with 23 APEG 1.0% is so high that some practical problems could be expected making thus necessary a strict mixing water adjustment. For all mixtures (L-O, and L-M-O) the addition of SP (except PCE1) considerably increased the setting time.

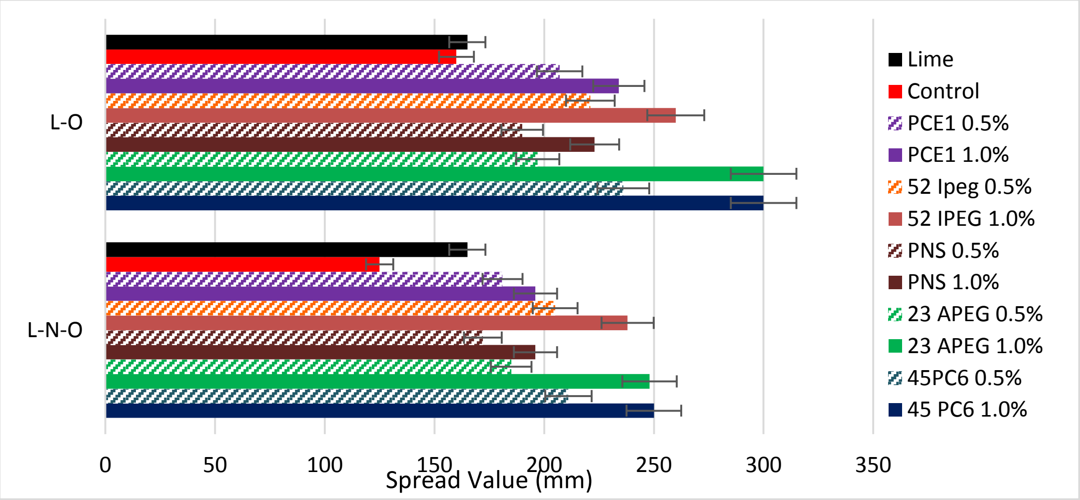


Figure 1. Fluidity of the different mixes

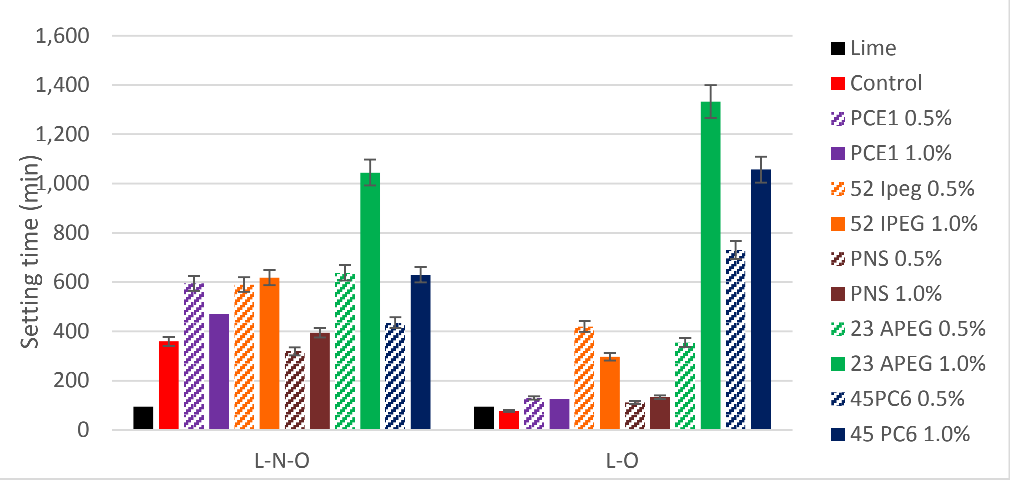


Figure 2. Workability of the different mixes

Compressive Strengths

The mechanical strengths increase over time due to the carbonation process, resulting in the formation of $CaCO_3$. Accordingly, on average, the highest values of compressive strength were obtained at long-term curing times, usually after 91 curing days (Figure 3 and 4). For the control mix L-O at 91 curing days, without the addition of the SPs, its compressive strength was highest in comparison with the other mixtures.

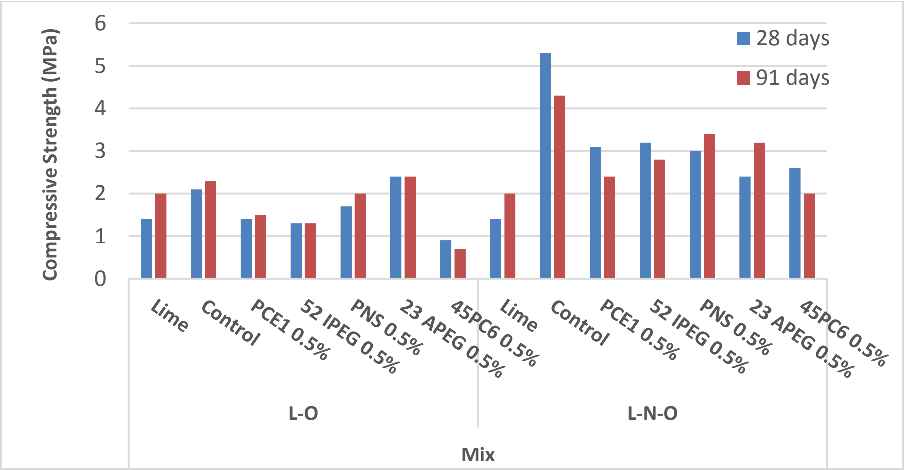


Figure 3. Compressive strength in the Hardened Mortars at different curing times (mixtures with 0.5% of superplasticizer)

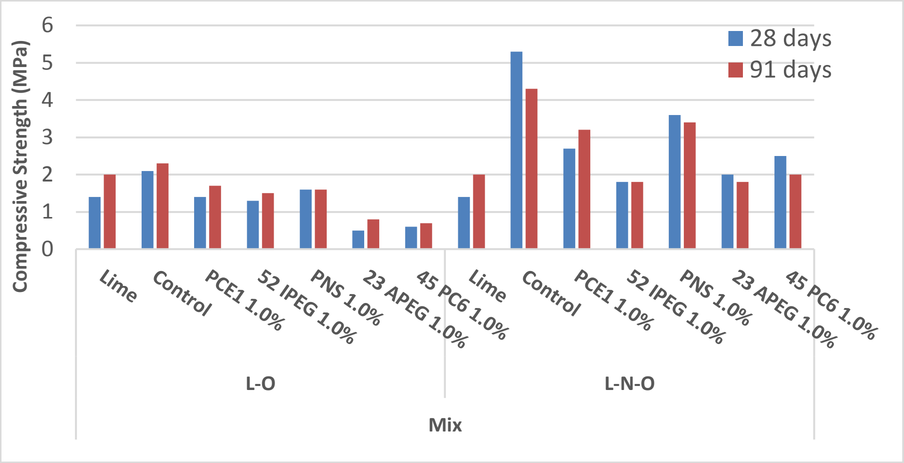


Figure 4. Compressive strengths at different curing times (mixtures with 1.0% of superplasticizer).

Hydrophobicity

The static water contact angle (WCA) and the water absorption time (i.e., the vanishing time of the water drop after its deposition, water drop lifespan, of interest for very porous substrates) were measured for the different grouts. The results are shown in Table 1.

In most samples water is fully absorbed after a certain period of time, as could be foreseen due to the very porous characteristics of the mortars' substrate. However it should be noted that, unlike a plain lime mortar, the WCA was able to be measured in all samples, thus indicating the water repellency brought about by the sodium oleate. In the curing time of 28 days the sample with excellent properties of water repellence is Lime + Oleate + Nanosilica +45PC6 1.0%+ TiO_2 and in 91 curing days is Lime + Oleate + Nanosilica +45PC6 1.0%+ TiO_2 this is because the drop was kept in the surface and the angle contact was higher than in the other samples.

Table 1. Water contact angle results

Mixture	Contact angle		Full Absorption of the water drop and disappearance in a short-time interval	
	28 days	91 days	28 days	91 days
Lime + TiO_2	-	-	Yes	Yes
Lime + Oleate+ TiO_2	26	23	Yes	Yes
Lime + Nanosilica+ TiO_2	29	32	Yes	Yes
Lime + Oleate + Nanosilica+ TiO_2	24	21	Yes	Yes
Lime + Oleate + PCE1 0.5%+ TiO_2	31	33	Yes	Yes
Lime + Oleate + PCE1 1.0%+ TiO_2	34	33	No	Yes
Lime + Oleate + 52IPEG 0.5%+ TiO_2	25	44	Yes	No
Lime + Oleate + 52IPEG 1.0%+ TiO_2	21	35	Yes	Yes
Lime + Oleate + PNS 0.5%+ TiO_2	22	27	Yes	Yes
Lime + Oleate + PNS 1%+ TiO_2	25	26	Yes	Yes
Lime + Oleate + 23APEG 0.5%+ TiO_2	37	17	No	Yes
Lime + Oleate + 23APEG 1.0%+ TiO_2	30	24	Yes	Yes
Lime + Oleate + 45PC6 0.5%+ TiO_2	23	20	Yes	Yes
Lime + Oleate + 45PC6 1.0%+ TiO_2	40	30	Yes	Yes
Lime + Oleate + Nanosilica +PCE1 0.5%	14	33	Yes	Yes
Lime + Oleate + Nanosilica + PCE1 1.0%+ TiO_2	44	28	Yes	Yes
Lime + Oleate + Nanosilica + 52IPEG 0.5%+ TiO_2	22	26	Yes	Yes
Lime + Oleate + Nanosilica +52IPEG 1.0%+ TiO_2	28	23	Yes	Yes
Lime + Oleate + Nanosilica +PNS 0.5%+ TiO_2	9	17	Yes	Yes
Lime + Oleate + Nanosilica +PNS 1.0%+ TiO_2	21	24	Yes	Yes
Lime + Oleate + Nanosilica +23APEG 0.5%+ TiO_2	44	42	No	Yes
Lime + Oleate + Nanosilica +23APEG 1.0%+ TiO_2	40	42	Yes	Yes
Lime + Oleate + Nanosilica +45PC6 0.5%+ TiO_2	16	20	Yes	Yes
Lime + Oleate + Nanosilica +45PC6 1.0%+ TiO_2	46	28	No	Yes

Photocatalytic activity (NO abatement)

In the current research work, photocatalytic efficiency of lime-based mortars was investigated as a measurement to estimate the potential self-cleaning performance. Photocatalytic studies were carried out to assess the effect of TiO_2, nanosilica, oleate, and different types and percentages of superplasticizers in limes-based mortars that had a different hardening time (28 and 91 days). The profiles of NO, NO_2 and NOx abatement measurements over time were obtained according to these studies (Figure 5). All samples showed similar behaviour in three periods of NO profile: in the absence of UV radiation (10 min), under UV radiation (30 min) and during the last 10 min when the UV radiation was off. First, the concentration of NO was kept constant. In the second stage, the decrease in NO concentration attained its maximum value and became constant. This was the consequence of the NO oxidation that took place due to a photocatalytic process on the surface of TiO_2 active sites. In the last stage, the NO concentration returned to its beginning value. For the NOx profile, the same behaviour was observed. The NO_2 (by-product of the NO oxidation) gas profile increased under UV radiation similar to previous studies on lime-based photocatalytic mortars.

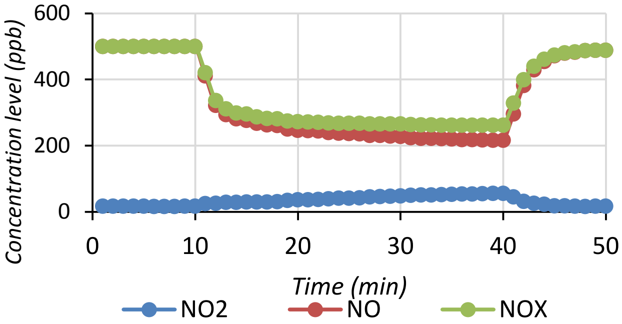


Figure 5. Profiles of NO, NO_2 and NO_x abatements for mortar with 1 % percentage of 45PC6 superplasticizer and nanosilica-free (91 days hardening)

Results revealed that presence of TiO_2 in lime-based mortars helped to better remove NO. Generally speaking, the presence of superplasticizers improved the NO reduction under UV irradiation. In this way it could be said that the different SPs enhanced the self-cleaning process. As shown in Figure 6, the percentage of the NO removal was commonly higher in SP-bearing samples after 91 curing days. Some contradictory values of NO abatement with some superplasticizers were observed for 28-days aged samples. The rates of NO removal were lower than that of control sample. 28 curing days might not be enough for lime-based mortars to show the PCO efficiency (Figure 6).

Samples with 0.5 % SPs after 28 days of curing showed similar efficiency of NO reduction (values of 43-50 %), except 23APEG that showed the lowest value (38 %). When samples with 1.0 % SPs were tested, the NO removal rates of PCE1 and 45PC6 yielded 47 % and 46%, respectively, but the rest of superplasticizers presented lower values (35-39 %) than that of the control sample.

After 91 days of curing (samples with 0.5% SP), the NO abatement values were increased for all samples with SP in comparison with control sample (NS-free samples). For samples with NS the presence of SPs improved the NO abatement (except for 52IPEG sample).

In the mixture L+ NS+ O samples with 0.5 % percentage SPs with 28 days hardening time, the range of remotion was 42-46 % in all superplasticizers except for PNS (34 %). Then at 91 hardening days, values were similar in PCE1, PNS, 23APEG and 45PC6 superplasticizers (43-46 %); in this case, value of 52IPEG was measured lower than control sample. With 1 % percentage of SPs in the same mixture, for the 28 days hardening time, all samples except for 52IPEG had the similar reduction values of 36-43 %. 52IPEG showed the same value with control sample. For 91 days, PCE1, 23APEG and 45PC6 presented the best values between 45 %, 48 % and 51 %, respectively. The other superplasticizers showed lower values than control sample.

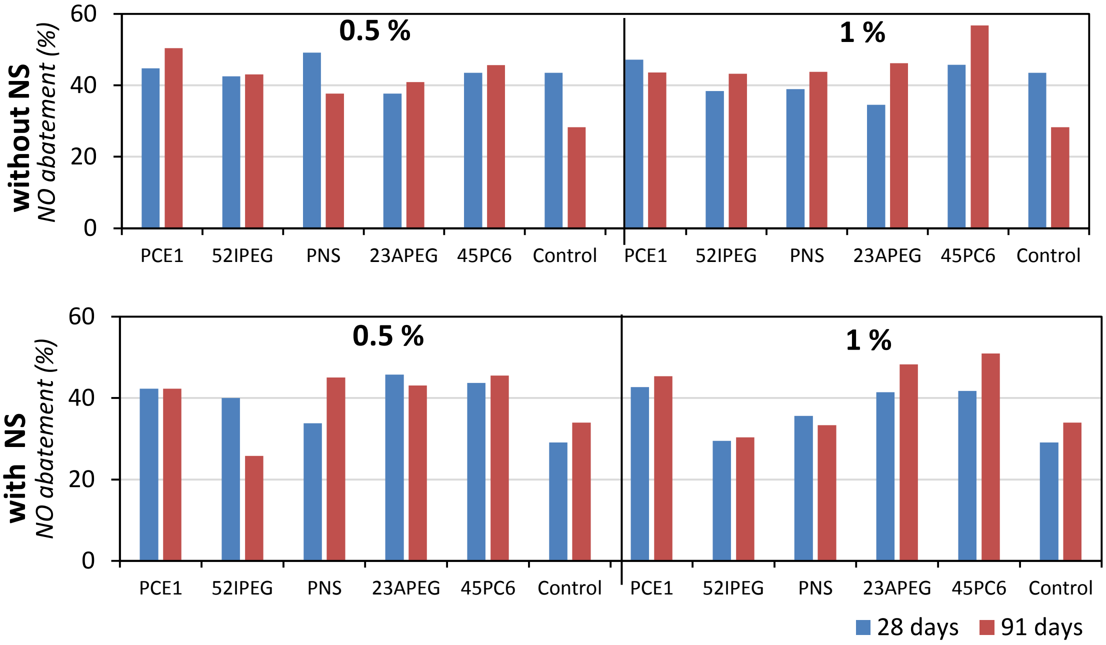


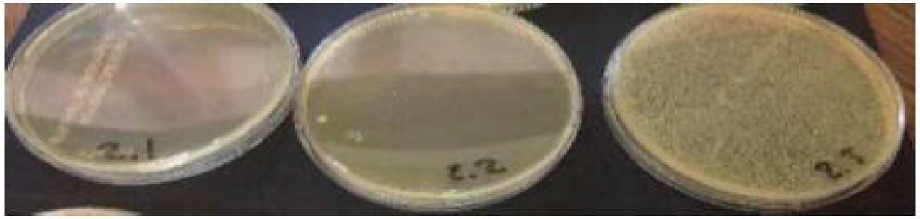
Figure 6. Percentages of NO abatement

Superplasticizers, mainly 45PC6 and PCE1, reduced the agglomeration of the nanoparticles of the photocatalytic additive and increased the potential self-cleaning characteristic of samples after 91 curing days. 45PC6 superplasticizer (1 %) with and without nanosilica exhibited a very remarkable NO removal rate (51 % and 57 %). It could be said that the efficiency of 45PC6 superplasticizer without nanosilica was better than the one with nanosilica when it was compared with control samples, probably as a consequence of the pozzolanic reaction that gave rise to the formation of a denser microstructure with a pore size reduction. These results were similar to the previous works dealing with the NOx abatement in lime-based systems.

Biocidal study

Once the photocatalytic studies were made, the samples were submitted to a biocidal study, and the results are gathered in Table 2.

Table 2. Results of biocidal study

Name of Sample	Photographs of the bacterial colonies form after peeling off the cylinder.	Pseudomonas Fluorescens presence
Lime		YES
Lime + Oleate		YES
Lime + Oleate + Nanosilica		YES
Lime + Oleate + Nanosilica+ TiO_2 Lime + Oleate + Nanosilica+ TiO_2+PCE1 0.5% Lime + Oleate + Nanosilica+ TiO_2+52IPEG 0.5% Lime + Oleate + Nanosilica+ TiO_2+PNS 0.5% Lime + Oleate + Nanosilica+ TiO_2+ 23APEG 0.5% Lime + Oleate + Nanosilica+ TiO_2+45PC6 0.5% Lime + Oleate + Nanosilica+ TiO_2+PCE1 0.5% Lime + Oleate + Nanosilica+ TiO_2+52IPEG 1.0% Lime + Oleate + Nanosilica+ TiO_2+PNS 1.0% Lime + Oleate + Nanosilica+ TiO_2+ 23APEG 1.0% Lime + Oleate + Nanosilica+ TiO_2+45PC6 1.0%		The behavior was the same in every TiO_2-bearing sample: the growing of *Pseudomonas Fluorescens* was fully inhibited

As can be seen in Table 2, the growing of *Pseudomonas Fluorescens* was noticeable in control lime-based rendering mortar and decreased (less CFU) for renders composed of nanosilica and oleate. Maybe the hydrophobicity of the surface hampered the microbiological colonization. No appearance of bacterial colonies was observed in all the samples that contain titanium dioxide in the mortar's formulation.

From these results it was not possible to establish the influence of the superplasticizer on the biocidal effect in the samples, since all TiO_2-bearing samples totally hindered the bacterial colonization. Further studies will intend to increase the number of colonies in each sample and controlling the microbiological growth over time.

Conclusions

The study on these new lime-based rendering mortars with TiO_2 focused on the efficiency of self-cleaning (measured as photocatalytic efficiency) and biocidal capacities of these renders to be used for the preservation of the Built Heritage.

To this aim, TiO_2, a water repellent agent, a pozzolanic additive and superplasticizers were combined with calcitic air lime. Compatibility between the admixtures and enhancement of different properties were assessed. Render mortars were seen to efficiently remove *Pseudomonas Fluorescens* proving the biocidal ability in comparison with plain lime-based renders. Hydrophobicity of the samples was generally increased, minimizing the detrimental effect of water uptake- Superplasticizers seemed to increase the photocatalytic efficiency (NO abatement) preventing TiO_2 particles from agglomeration, but all the renders showed photocatalytic activity and thus a potential self-cleaning capacity which might significantly reduce the maintenance and cleaning costs by preventing damage of the use of chemicals or abrasive agents in restoration works.

According to the results obtained in fluidity and workability time tests, the composition of these renders should be optimized for the real application of these mortars. The best mix with the highest water repellency was Lime + Oleate + Nanosilica + 45PC6 1.0% + TiO_2, as it showed the greatest WCA after 91 curing days.

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