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# Assessing the self-healings properties of nano -Ca(OH)<sub>2</sub> – TiO<sub>2</sub> – ZnO materials used in monuments conservation works

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**Abstract.** Consolidates based on Ca(OH)<sub>2</sub> have been prepared as macro- and/or nanoparticles dispersed in different alcohols, regardless of the precursor nature. Their efficiency is related to the small dimensions of the particles and the dispersion media, which allows their penetration into the deteriorated material substrates, as well as to an increased reactivity towards CO<sub>2</sub>. Besides the consolidating effect there is a strong need for the newly developed materials to also tackle other properties like self cleaning and antimicrobial activity, especially with regards to white monuments. In this context the present work highlights the effect of treating with stable alcoholic suspension containing nano - Ca(OH)<sub>2</sub> – TiO<sub>2</sub> – ZnO the physical support models consisting of mortar cubic samples from hydraulic / aerial lime, a commonly used materials in consolidation works.

## 1. Introduction

When talking about cultural heritage, all the focus should be on the conservation so that our future generations can enjoy of this inestimable value, but also so that our roots and the artistry of our ancestors to be known and permanently anchored into the present.

From a technical perspective, the main challenge is to develop a consolidator which fits with the original material, binding it effectively, without harming it or the rest of the structure. Related to this topic there are many researches demonstrating that the nano-lime based materials are suitable to consolidate the decayed limestone and plasters, satisfying the performance criteria expressed above, offering theoretical advantages over traditional materials such as lime water and lime grouts [1-3].

Consolidates based on calcium hydroxide have mainly been prepared as macro- and/or nanoparticles dispersed in different alcohols, whether they were obtained from pure precursors or agro-industrial waste [4-6]. Their efficiency as consolidates is related to the particles dimensions and the used dispersion media, facilitating their penetration into the deteriorated material substrates, but also to an increased reactivity towards carbon dioxide [2, 7, 8].



The newly developed materials should also present other properties, such as self cleaning and antimicrobial activity, especially when considering white facades and statues. Therefore, some recent studies have focused on other innovative approaches in order to fulfill some of these characteristics. The investigations analyze the possibility of embedding the photocatalytic nanoparticles in polymeric matrices to obtain bioactive coating, with self-cleaning, antimicrobial and consolidating properties for preservation of marble stone monuments [9, 10]. A strong candidate which successfully fulfills these requirements is nanosized titanium dioxide. Through its immobilization within a layered-structure material, a  $\text{TiO}_2$ -inorganic nanocomposite can be obtained [11]. Additionally, a  $\text{TiO}_2/\text{Zn-Al}$  nanocomposite powder with demonstrated photocatalytic properties could improve the compatibility between the photocatalytic coating and the substrate [12].

In the present study, a stable alcoholic suspension containing nano -  $\text{Ca(OH)}_2 - \text{TiO}_2 - \text{ZnO}$  was obtained. In this purpose nano- $\text{Ca(OH)}_2$  was obtained starting from eggshells, which were dissolved in 9% HCl solution. The  $\text{TiO}_2$  was obtained by sol-gel synthesis starting from titanium tetrachloride and ethanol. The zinc oxide was synthesized starting from  $\text{Zn(NO}_3)_2$  tetra hydrate which by reaction with NaOH led to  $\text{Zn(OH)}_2$  formation. In order to assess the beneficial actions of these chemical compounds, physical support models were obtained consisting of mortar cubic samples from hydraulic / aerial lime, used for restoration works of monuments. The physical-mechanical properties of the support models before and after treatment with  $\text{Ca(OH)}_2$ -based nanomaterials were evaluated through mechanical compression tests, demonstrating the positive strengthening effect of the nanomaterials.

## 2. Materials and methods

In order to assess the self healing capacity of  $\text{Ca(OH)}_2\text{-TiO}_2\text{-ZnO}$  nano-powders exerted in binding hydraulic materials, the study was divided into two comprehensive stages.

### 2.1. Obtaining of alcoholic suspension containing nano $\text{Ca(OH)}_2 - \text{TiO}_2 - \text{ZnO}$

In the first stage a stable alcoholic suspension was obtained which contains  $\text{Ca(OH)}_2 - \text{TiO}_2 - \text{ZnO}$  nano-powders. Nano- $\text{Ca(OH)}_2$  was obtained starting from the eggshells which were dissolved in 9% HCl solution. When the eggshell powder was completely dissolved, the  $\text{CaCl}_2$  solution was filtered under vacuum to remove the organic membranes. The nano- $\text{Ca(OH)}_2$  was obtained by precipitation of  $\text{CaCl}_2$  (aq) with NaOH 12M solution. The resulted white precipitate was washed with distilled water, in excess, and dried in an oven at  $T = 100^\circ\text{C}$  for two hours.

In parallel the  $\text{TiO}_2$  was obtained by sol-gel synthesis starting from titanium tetrachloride ( $\text{TiCl}_4$ ), ethanol (EtOH) of absolute purity of 99.9% and sodium hydroxide.  $\text{TiCl}_4$  was dropped into a 1:1 water/alcohol mix, which was maintained on ice bath, under vigorous stirring. The concentration of  $\text{Cl}^-$  ions was reduced by increasing the pH from 0 to about 2.5-3, by dropping sodium hydroxide solution under vigorous stirring, determining thus the gel formation. The matured gel was subjected to repeated cycles of washing - centrifugation with a mixture of ethanol + distilled water in volumetric ratio of 1:1 until the final product was considered free of impurities. The resulted material was then autoclaved at  $80^\circ\text{C}$  for 24 hours and after that heat treated at  $400^\circ\text{C}$ . After obtaining, 1g of nano- $\text{TiO}_2$  was resuspended in 200 ml of ethanol solution, containing 2 g of nano- $\text{Ca(OH)}_2$  and vigorously mixed for 1 h to obtain a stable suspension of nano- $\text{Ca(OH)}_2 - \text{TiO}_2$ .

Zinc oxide ( $\text{ZnO}$ ) was synthesized starting from  $\text{Zn(NO}_3)_2$  tetra hydrate which by reaction with NaOH led to  $\text{Zn(OH)}_2$  formation. After maturation, the white precipitate was filtered and washed with a mixture of distilled water and ethanol, at a 1:1 volumetric ratio, and dried in oven at  $70^\circ\text{C}$ . After calcination at  $600^\circ\text{C}$  for 1 hour, 1 gram of nano- $\text{ZnO}$  was resuspended in the solution containing  $\text{Ca(OH)}_2\text{-TiO}_2$  binary mixture, thus resulting a stable alcoholic suspension containing nano  $\text{Ca(OH)}_2 - \text{TiO}_2 - \text{ZnO}$ .

**2.2. Obtaining of physical support models by using binding materials specific to historical monuments and assessing the self healing properties**

In the second stage of work physical support models were obtained consisting of mortar cubic samples from hydraulic lime, NHL 3.5, respectively aerial lime, used for restoration works of monuments. The samples were made with sand/binder ratio of 1:3, respectively water/binder ratios between 0.6 - 0.8 (table 1). The samples were kept in the molds for 1 day, and after demolding, up to 28 days in the laboratory atmosphere.

After 28 days the mortar specimen were subjected to a controlled cracking program by freeze-thaw cycles, using a climatic chamber Discovery 800.

**Table 1.** The composition of physical support models

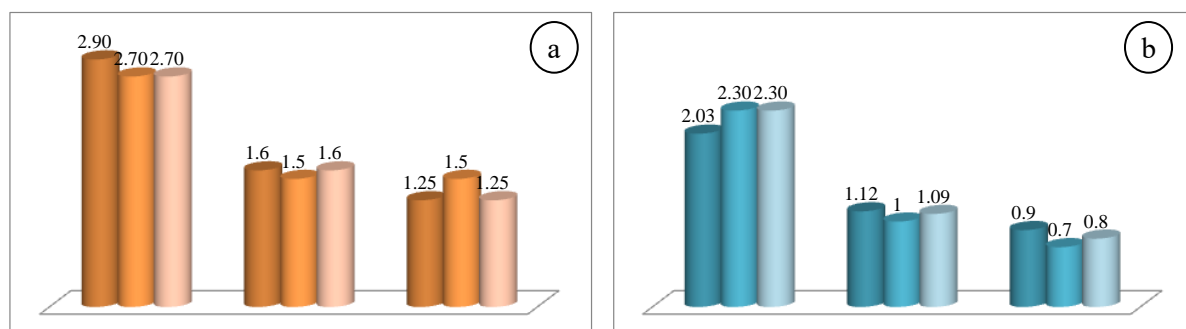
Sample	Standardised aggregates [g]	Binder [g]	Water [cm <sup>3</sup> ]
P1	1350	450 – NHL 3.5	270
P2	1350	450 – aerial lime	315
P3	1350	450 – aerial lime	360

It was set a degradation program for 5 days with a cyclic variation of temperature and humidity (T = -40... + 40 C, for 4h and 0.5h stabilization time, respectively R.H. = 0 - 90% with the same preset time). After being subjected to this program, the mortar specimens were treated with stable alcoholic suspension containing nano Ca(OH)<sub>2</sub> - ZnO - TiO<sub>2</sub>, by pipetting, the surfaces of the samples being saturated with liquid and left to dry for 24 hours in the laboratory atmosphere, this operation being carried out during 72 hours (3 coating cycles), then kept under the same conditions for a period of 28 days.

This treatment was performed to evaluate the self-healing properties of nanomaterials injected into the binder structure. The mortar specimens' resistance was determined after each currying condition (initial, after the freeze-thaw cycles and after the treatment with nanomaterials) by compressive strengths determinations and the microstructure evolution by field emission scanning electron microscopy (FE-SEM) by using a HITACHI SU 70 scanning electron microscope.

**3. Results and discussions**

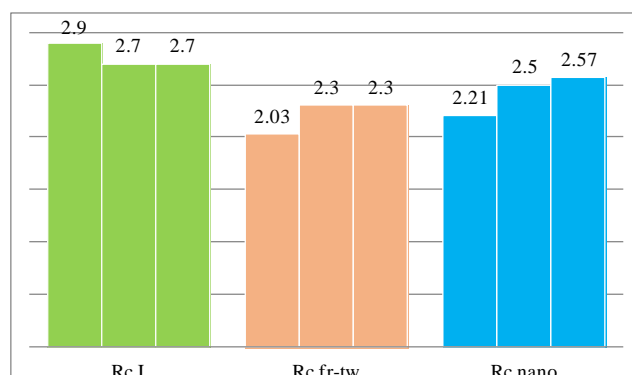
The behaviour of lime mortar specimens in different curing conditions, assessed by compressive strength evolution, is presented below. Thus, in Figure 1 are presented the compressive strength of mortar specimens after 28 days of hardening, and compressive strength of mortar specimens after freeze-thaw cycles respectively.



**Figure 1.** a) Compressive strength (MPa) of mortar specimens after 28 days of hardening, b) respectively compressive strength of mortar specimens after freeze-thaw cycles.

Mortars based on hydraulic/aerial lime, intended for the restoration of monuments, are weak mortars in terms of mechanical resistance, but the compressive strength is not the main characteristic since they are used for the restoration of the superficial layer of historical monuments. It can be seen that for the chosen compositions the best results were recorded on the mortars made with NHL 0.5 hydraulic lime, (P1 composition), whose initial strengths were between 2.7 and 2.9 MPa. The freeze/thaw cycles led to a decrease in strength by approx. 30% of the initial value, reaching values of 2.03 and 2.3 MPa respectively. The higher water/binder ratio (0.8) is reflected in the strengths of mortars based on aerial lime, which have values between 1.25 – 1.5 MPa, and after the freeze-thaw treatment reaching values of 0.7 - 0.9 MPa.

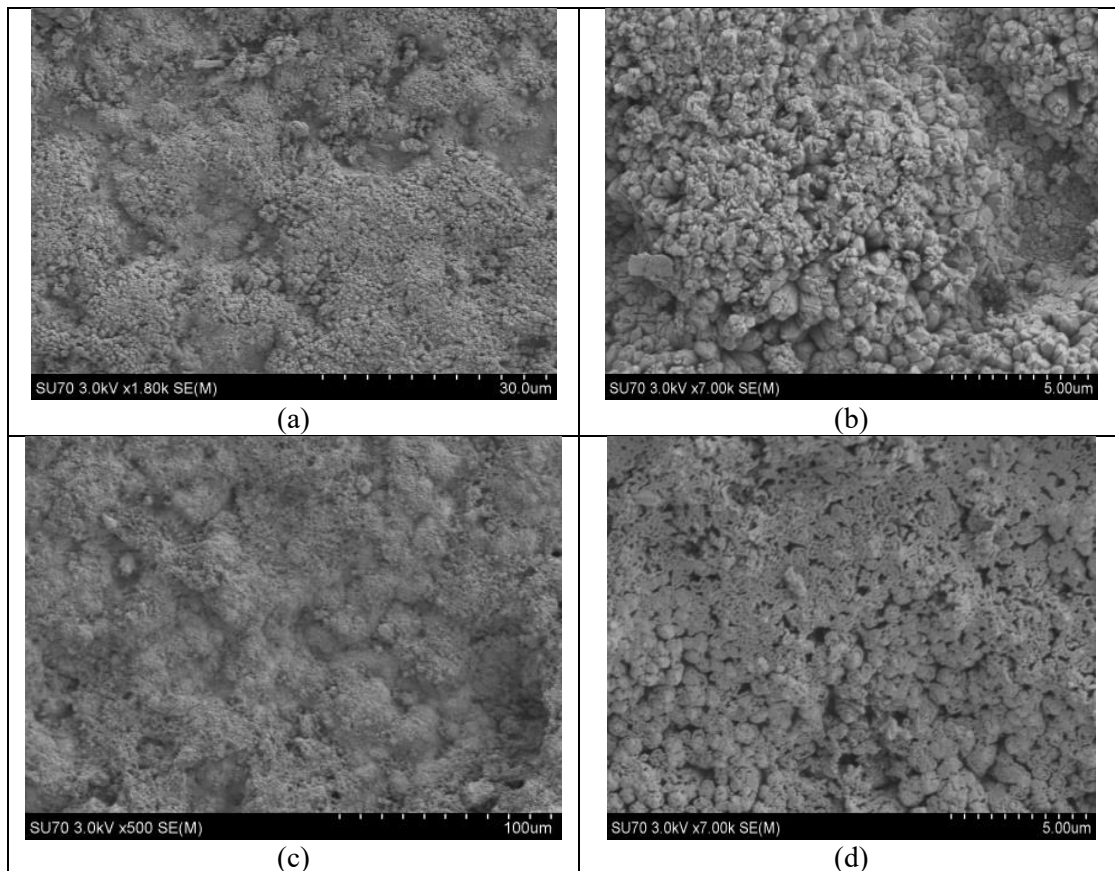
The evolution of mechanical strengths after the nanomaterials treatment is highlighted in Figure 2. It is presented only the results obtained for the P1 mortar specimens since it recorded the best results.



**Figure 2.** The values of P1 compressive strengths presented comparatively: the initial sample (RcI), the degraded sample controlled by the freeze-thaw program (Rc fr-tw), respectively, the samples subjected to the gelivity test and treated with stable alcoholic suspension containing nano  $\text{Ca}(\text{OH})_2 - \text{TiO}_2 - \text{ZnO}$ , (Rc nano).

As can be seen, the compressive strengths have registered an increase in values, with approx. 10%, after the surface treatment with nanomaterials. Thus, the average strength of the treated samples,  $Rc\ nano = 2.43\text{MPa}$ , is higher than that of the controlled degraded samples,  $Rc\ fr-tw = 2.21\text{MPa}$ . This behavior can be explained by the densification of the structure on the surface of the mortar samples through the carbonation of nano- $\text{Ca}(\text{OH})_2$ , respectively the filler effect that the nanometric particles exert in the composition of the coating solution, simultaneously with the advancement of the hydration reaction of the hydraulic lime compounds.

The self-healing properties of nano- $\text{Ca}(\text{OH})_2$  based materials were assessed by scanning electron microscopy, by analyzing the mortar specimens structure before and after the treatment, the results being presented in Figure 3.



**Figure 3.** SEM images of P1 specimen surface, before, a) and b) and after the treatment with nano- $\text{Ca(OH)}_2\text{-TiO}_2\text{-ZnO}$ , c) and d), presented at different magnifications.

As it can be seen from Figure 3, there are cracks on the surface of the untreated samples that appeared as a result of the drying process. The SEM analyses exhibit a porous layer with large open pores and with well-defined grains, which presented edges and corners (figure 3a and b). After the treatment with the stable alcoholic suspension containing nano- $\text{Ca(OH)}_2\text{-TiO}_2\text{-ZnO}$  the surface becomes smoother and the space between the granules, initially occupied by air, is filled with hydro compounds resulted from the hydration reaction of hydraulic lime, respectively carbonates, resulted in the presence of  $\text{CO}_2$ . Thus, the self-healing effect is in this case very well highlighted.

#### 4. Conclusions

In the first part of the present work, the stable suspension containing nano -  $\text{Ca(OH)}_2 - \text{TiO}_2 - \text{ZnO}$  was obtained by vigorous mixing the three components of the ternary system in an aqueous solution, being added in mass report of 2:1:1. In this purpose, all components were synthesized under laboratory conditions, either from waste or pure chemical precursors. Thus, nano- $\text{Ca(OH)}_2$  was obtained from eggshells, which were dissolved in 9% HCl solution.  $\text{TiO}_2$  nanoparticles were obtained by sol-gel synthesis starting from titanium tetrachloride and the ethanol, and ZnO was synthesized starting from  $\text{Zn(NO}_3)_2$  tetra hydrate which by reaction with NaOH led to  $\text{Zn(OH)}_2$  formation.

The physical-mechanical properties of the support models before and after treatment with  $\text{Ca(OH)}_2$ -based nanomaterials were evaluated through mechanical compression tests, demonstrating the positive strengthening effect of the nanomaterials in lime mortar specimens (as used in historical monuments). The micro-structural analysis of the surfaces of the mortar specimens treated and untreated with stable suspensions based on nano- $\text{Ca(OH)}_2$  performed by SEM analyses revealed also the self-healing effect highlighted by smooth surfaces of the samples due to the newly formed compounds through the  $\text{Ca(OH)}_2$

carbonation, respectively with hydro compounds resulted from the hydraulic lime hydration reaction, and on the other hand, the filler effect exerted by the nanometric particles on the material.

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