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Original article

Silica nanoparticles (SiO_2): Influence of relative humidity in stone consolidation

Ainara Zornoza-Indart[a,*], Paula Lopez-Arce[a,b]

[a] Instituto de Geociencias IGEO (CSIC, UCM), C/José Antonio Nováis 2, 28040 Madrid, Spain
[b] Université de Cergy-Pontoise, Géosciences et Environnement department, 5, mail Gay-Lussac, rue d'Eragny, Neuville-sur-Oise, 95031 Cergy-Pontoise cedex, France

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ABSTRACT

The influence of relative humidity (RH) has been determined in SiO_2 colloidal nanoparticles, to study their efficacy as a consolidating product by means of the physical changes in the hydric and mechanical properties produced in a siliceous-carbonate stone from a historic building (XVI century) with signs of degradation. Therefore, diverse analytical techniques have been used for the product characterization (TEM-EDS, ESEM-EDS, XRD, DTA-TG, spectrophotometry) together with micro-destructive (SEM, micro-drilling resistance) and non-destructive petrophysical tests (hydric tests, ultrasonic velocity, adhesion and microhardness tests) for the characterization of the stone. The precursor water colloidal nanosilica, when is initially exposed to high RH environments, forms agglomerated spherical nanoparticles of amorphous silica, that holds a higher amount of adsorbed water and lower amount of silanol groups on the surface, compared to samples exposed to lower RH. This final product behaves in a similar way than a silica gel, when is exposed once again to lower and higher RH, as a reversible hydration–dehydration process of adsorbed water. Related to the efficacy as a consolidant, the results show differences both, in surface changes, decreasing the amount of released material from the substrate and increasing its surface hardness, as in the interior of the porous structure, increasing absorption and desorption water capillarity rates, ultrasonic velocities and drilling resistance, showing high efficiency and less adverse aspects at lower RH. However, this effect and the possible decay caused by repeated cycles of hydration–dehydration of the silica gel inside the porous of the stone should be assessed in order to determine its durability.

1. Research aims

The goal of this research is to determine the influence of relative humidity in aqueous solutions of colloidal silica (SiO_2) nanoparticles and to study their efficacy as a consolidating product, by means of the physical changes, hydric and mechanical properties, produced in a siliceous-carbonate stone substrate from an historic building with signs of degradation. For this purpose, advanced analytical techniques are used in the characterization of the product, and non-destructive or micro-destructive petrophysical tests for the stone characterization, determining so, the behavior of nanosilica and the most suitable environmental conditions of application.

2. Introduction

The artistic-historical heritage in addition of supposing a significant sociocultural legacy, is currently one of the most important assets in the industry related to the field of tourism, with a significant economic value. Due to the passage of time and the exposure to different weathering process, nowadays the cultural heritage conservation becomes necessary for its future continuation. For this reason, research on more effective, and stable with the passing of time, new conservation treatments, is in these days one of the most important fields in cultural heritage conservation sciences. In the search of new products to solve the negative aspects caused by traditional ones, the application of inorganic nanoparticles in heritage conservation has generated novelty treatments, especially in the conservation of construction materials (mortars, building and ornamental stone, wall paintings, ceramics...). Cleaning agents, biocides, consolidants and hydrorepellents, products for extracting salts or to generate self-cleaning surfaces, are nowadays an innovative research field worldwide. In the development of

* Corresponding author. Tel.: +34 913944903; fax: +34 915442535.
E-mail addresses: ainarazornoza@pdi.ucm.es (A. Zornoza-Indart), paula.lopez-arce@u-cergy.fr, plopezar@geo.ucm.es (P. Lopez-Arce).

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consolidating products applied to stone materials, the application of nanotechnology has allowed developing new products to consolidate stone materials by the addition of colloidal nanoparticles to alkoxysilanes products [1–4], creating nanostructured materials from alkoxysilanes [5], developing inorganic products acting both, as sulfates removal and consolidants [6–8] or creating products based on nanoparticles like calcium hydroxide [$Ca(OH)_2$], magnesium hydroxide or silica nanoparticles (SiO_2), sold as totally compatible with the substrate.

In the studies of $Ca(OH)_2$ nanoparticles, the environmental conditions (relative humidity) play a significant role in the carbonation process of these nanoparticles and in the final mineralogical phases, conditioning the physical properties in a short- and longer-term [9–11]. However, the consolidating product based on SiO_2, has been less studied, requiring more research works to evaluate the necessary variables to take into account in the final physical properties and in the efficacy after its application in different types of materials.

Nanosilica has been applied in the construction field as an additive of concrete, to increase cohesion, compression and flexural resistances, and to reduce the porosity after setting, increasing the durability [12–15]. As a restoration treatment for stone materials, nanosilica has been applied mixed with calcium hydroxide nanoparticles to accelerate setting times, to consolidate highly porous gypsum and as protective film for pigments [16]. Another study carried out in fresco paintings artificially deteriorated showed the importance of application conditions and the porosity of the substrate [17]. Nanosilica has also been applied to consolidate the First order loggia capitals from Pisa Tower (Carrara marble) [18] and the highly porous limestone, known as “Gentile stone” [19]. This product has also been used in archaeological sites, as the consolidation of plastered surfaces in an industrial archaeological site (XIX century) in Italy, comparing silica nanoparticles (Syton® X30), calcium hydroxide nanoparticles (Nanorestore®), and cellulose poultices with oxalate and ammonium phosphate [20]. These silica nanoparticles were also used mixed with crushed stone, in the Precolombine archaeological site of Tajin (Mexico), to reintegrate the volume of the areas where the “intonaco” was lost [21].

In the field of painting restoration, these have also been applied to protect the pictoric layers by the *layer-by-layer assembly* technique, that consists in covering pigments by successive protective layers of nano-SiO_2 [22], studying later the protective effect and the increase of durability against the external agents produced in organic pigments [23].

In spite of the research already carried out, the real application of these new products based on nanoparticles is still scarce on restorers behalf, because still remain non solved key aspects until these could be used in situ, related to their efficacy and the results obtained in a long-term, taking into account environmental conditions and durability.

3. Materials and methods

3.1. Materials and sample preparation

3.1.1. SiO_2 nanoparticles

Nano Estel®, is an aqueous colloidal dispersion of silicon dioxide with nanometric dimensions, ca. 10–20 nm, lower than the acrylic micro-emulsions (40–50 nm) and the alcoholic dispersions of $Ca(OH)_2$ nanoparticles (between 60 and 130 nm). According to the technical datasheet, this is presented as a consolidating product for siliceous rocks, as an inert binder of mortars and renders, and as affixer of powdering pigments in wall paintings by the silica gel formed as a final product (similar to that obtained by ethyl silicates reactions) once the water is evaporated. It can be used under conditions where ethyl silicate is not convenient, i.e. situations with little time available, or in the presence of high humidity values, free water or damp surfaces [24,25]. For the characterization analyses, this was diluted in deionized water down to 5 g/L and then exposed in 4 containers, used as climatic chambers at different relative humidity (RH) conditions (20 mL in each chamber) during 15 and 30 days. A concentration of 5 g/L was used in order to be compared with other current innovative commercial consolidating products based on nanoparticles, such as Nanorestore®, which is based on $Ca(OH)_2$ nanoparticles dispersed in 2-propanol. Furthermore, a low concentration allows an easier characterization of the product by means of transmission electron microscopy (TEM), since higher concentrations give rise to an agglomeration of the nanoparticles that makes difficult to measure the size and interparticles distances of the nanoparticles obtained from the TEM images. To control and keep constant RH in the chambers, water and the RH in the equilibrium (RHeq) of different saturated salt solutions was used (all at 20 °C): to simulate a dry environment (33.07%, using $MgCl_2$), half humid environment (69.90% using KI), humid environment (75.47% using NaCl) and very humid environment (100% using H_2O). To avoid condensation and to make easier the evaporation of the solution small holes were done in the cover of the climatic chambers. Environmental control devices, i-buttons® model DS1923-F5 were introduced in each chamber and placed in the laboratory room to measure T and RH during the 30 days experiment, using the software OneWireViewer version 3.04. The final RH values obtained in each chamber at 20 °C, were:

- dry environment ($45 \pm 5\%$);
- half humid ($65 \pm 10\%$);
- humid ($80 \pm 3\%$);
- very humid environment ($95 \pm 4\%$).

3.1.2. Stone specimens

Additionally, this product was applied as a consolidation treatment of sedimentary rocks, with siliceous and carbonate composition, broadly used in historic monuments from the Mediterranean Basin, with the aim of give them cohesion back and slow down weathering. These rocks are bioclastic sandstones (calcarenites), with abundant porosity, big pore sizes and partially cemented with calcite [26].

Cubic specimens ($5 \times 5 \times 5$ cm) from detached and decayed calcarenite ashlars from the Spanish Fort of Bizerta, Tunisia (XVI century) were used to carry out the laboratory work (Fig. 1a). This stone type shows high degree of decay due to significant honeycomb weathering, decohesion and loss of material by salt crystallization from marine spray (Fig. 1b).

Two exposure environments, dry RH (achieving $40 \pm 2\%$ by $MgCl_2$) and very humid RH ($95 \pm 2\%$ by H_2O) were selected to consolidate the stone samples during 30 days, and to determine so the influence of environmental conditions in the efficacy of the consolidation process. Following the technical data sheet from the manufacturer, the product was diluted one time in order to obtain a concentration of 150 g/L (15% dry residue). The amount of product necessary to consolidate each specimen was calculated by means of the total amount of water absorbed at atmospheric pressure (37 ± 2 mL), deciding to finally applied 40 mL of product by brush (Fig. 1c).

3.2. Analytical techniques and experimental procedure

3.2.1. SiO_2 nanoparticles analyses

The characterization of the SiO_2 nanoparticles has been studied after 15 and 30 days exposure to the different environmental conditions, by transmission electron microscopy (TEM) with energy dispersive X-ray spectroscopy (EDS) to study the crystallinity and