Construction and Building Materials 116 (2016) 188–202

Contents lists available at ScienceDirect

Construction and Building Materials

journal homepage: www.elsevier.com/locate/conbuildmat

Consolidation of a Tunisian bioclastic calcarenite: From conventional ethyl silicate products to nanostructured and nanoparticle based consolidants

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HIGHLIGHTS

- Differences in the consolidation effect and in the physical properties.
- Alkoxysilanes: produce a layer which occludes the pores and remains hydrophobic after 1 month.
- Nano $Ca(OH)_2$ and SiO_2 produce changes due to the creation of micropores.
- Nano SiO_2 in dry RH: moderate physical changes, less shrinkage and color changes.
- Nano $Ca(OH)_2$: barely change physical properties, lowest surface-internal consolidation effectiveness.

ARTICLE INFO

Article history:
Received 14 February 2016
Received in revised form 12 April 2016
Accepted 26 April 2016

Keywords:
Stone
Consolidation
Relative humidity
Ethyl silicate
Calcium hydroxide nanoparticles
Silica nanoparticles

ABSTRACT

Mediterranean calcarenite stones are exposed to several weathering processes related to the climate and environment, producing alteration features conducing to loss of cohesion in their structures. Samples of these building materials were collected from the Spanish Fort of Bizerte (Tunisia) to carry out laboratory tests in order to assess the consolidation effect of the nowadays most frequently used products and most innovative consolidation materials based in nanoparticles. Stone specimens were consolidated with the most employed alkoxysilane product (ethyl silicate), with a surfactant-templated novel sol-gel product (that avoids the tendency to crack) and with inorganic products based on calcium hydroxide nanoparticles ($Ca(OH)_2$) and silica nanoparticles (SiO_2) under very humid and dry environmental conditions. Samples were characterized by scanning electron microscopy, peeling test, superficial hardness, drilling resistance, water absorption by capillarity and under vacuum, water desorption and spectrophotometry, before and after one month of the application of the products to evaluate their consolidation effect under different environmental conditions. The results show great differences in the consolidation effect and in the changes produced in the physical properties of the substrate after using alkoxysilane products (even nanostructured) or products based in nanoparticles. In the case of alkoxysilane and nanostructured products, especially exposed to high RH conditions, the mechanical properties of the substrate, internal and surface, increase. In both cases a layer on the substrate which occludes the pores is generated maintaining a hydrophobic behavior after one month causing drastic changes in the hydric behavior with visually detectable aesthetic changes. In the case of inorganic nanoparticles, changes in the porosity of the substrate caused by the creation of micropores occur in both cases. In the case of SiO_2 nanoparticles, moderate physical changes occur in dry conditions resulting in less shrinkage and color changes. Finally, $Ca(OH)_2$ nanoparticles are the products with the lowest surface and internal consolidation effectiveness which barely change the physical properties of the stone.

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http://dx.doi.org/10.1016/j.conbuildmat.2016.04.114
0950-0618/

1. Introduction

In addition of the important socio-cultural legacy role, Cultural Heritage is nowadays one of the most important economic incomes related to the tourism industry. In spite of its huge economic value, the passage of time, as well as the exposure to diverse deterioration processes, heritage leads to the need of some kind of intervention for its conservation. In the research of more effective and more stable treatments, the application of nanomaterials (inorganic nanoparticles, nanocomposites and nanoporous structures) to the Cultural Heritage conservation has generated innovative treatments and procedures. These practices are applied particularly in the conservation of building materials from architectural heritage (i.e. mortars, plasters, stone materials, both with structural or ornamental purposes, ceramics) such as cleaning agents, consolidating products, biocides, water-repellent and self-cleaning surfaces, being nowadays the most important field on scientific conservation. From the mid 20th century, in the development of consolidating products applied to stone materials, the application of synthetic organic polymers (such as acrylic or epoxy resins) caused many drawbacks (incompatibility with the substrates, chromatic changes and long-term ageing). The most widely used stone consolidants over the past thirty years have undoubtedly been the alkoxysilanes (referred to in the literature as silanes, silicon esters, silicic acid esters, ortho silicates or alkyl silicates), being tetraethoxysilanes the most frequently type used by restorers also known as silicic acid tetraethyl ester, tetraethylorthosilicate, and mainly renowned as ethyl silicates or TEOS, i.d. partially polymerized tetraethoxysilane [1]. Silanes are hydrolyzed by water to form silanols, which then polymerize through a sol-gel process, in a condensation reaction to give a silicone polymer in which amorphous silica is obtained inside the porous structure of the stone. Although they have some advantages over organic consolidating products (including their low viscosity and high chemical stability) they have some drawbacks. For example, their tendency to crack, their temporal hydrophobic behavior and the stone substrate-gel incompatibilities. Regarding the influence of the environmental conditions during gel polymerization of alkoxysilanes, some authors remarked relative humidity as one of the most important variables affecting the process [1–3]. Wheeler et al. [4] have reported the successful use of silane coupling agents—compounds intended primarily to promote adhesive links between two materials of radically different chemical composition. Wheeler found two coupling agents that gave substantial strength increases to both limestone and sandstone, but at the expense of significant darkening [5].

The application of nanotechnologies allowed the development of new products for the consolidation of stone materials based on colloidal dispersions of inorganic nanoparticles obtaining more compatible and long-term stable products. Nanotechnology techniques are providing novel nanostructured products derived from alkoxysilanes enhancing their effectiveness and preventing their drawbacks.

In the case of inorganic nanoparticles, calcium hydroxide ($Ca(OH)_2$) nanoparticles are the most used products for the treatment of stone materials and wall paintings. When exposed to atmospheric carbon dioxide (CO_2), under relative humidity conditions, they react, producing calcium carbonate ($CaCO_3$) and releasing water as a result of the carbonation process. There are many known factors and conditions that control the precipitation of $CaCO_3$ polymorphs, such as pH, temperature, saturation, conductivity, and the presence of impurities and additives that determine mineral precipitation and phase transformations, together with morphological and structural changes. The variables that play a role on the $Ca(OH)_2$ nanoparticles carbonation and the resulting minerals are essential to the final physical properties of the stone, in short-term as well as long-term periods of time [6]. Many works refer that the best results are achieved by using $Ca(OH)_2$ nanoparticles applied under high relative humidity conditions [7–10] and, López-Arce and Zornoza-Indart [11] have concluded that, on diverse types of limestones, supplementary source of CO_2 favors and accelerates carbonation of $Ca(OH)_2$ nanoparticles improving the mechanical properties of stone substrates. Calcium hydroxide ($Ca(OH)_2$) nanoparticles have been applied to improve the petrophysical properties of lime mortars and carbonate stones, acting as a cementing product to avoid decohesion of construction and building materials [6,12] or to consolidate archaeological wall paintings [13].

Although there is fewer research in the case of the SiO_2 nanoparticles, their effectiveness in comparison with alkoxysilanes and $Ca(OH)_2$ nanoparticles consolidants on limestones [14–16], archaeological materials [17,18], historical mortars [19], and in ignimbrites [20] have been studied. Furthermore, Zornoza-Indart and López-Arce [21] studies confirm the influence of relative humidity on the silica gel generation.

In the case of nanostructured products from alkoxysilanes, Mosquera et al. [22] have designed a novel consolidating product in which the sol-gel transition occurs in the presence of a neutral surfactant (n-octylamine) using it as a template for the silica pores. This provides an efficient mean of avoiding cracking of the gel while it is drying inside the stone. As the gel cracking occurs, which is a consequence of the capillary pressure gradient through the porous network, a transparent gel is created. In this gel a uniform capillary pressure prevails, making coarser and uniform the pore size of the gel network (with a 80% of mesoporous size pores). The surfactant interacts weakly with the silica precursor by hydrogen bonds, allowing it to be removed by drying in ambient air. Regarding its application to stone material (biocalcarenite), it has been concluded that the surfactant is self-removed six months after its application [22]. Comparing the results obtained with commercial ethyl silicates (Tegovakon® V100) and the nanostructured product, in spite of the penetration depth through the stone is similar (about 4 cm), the nanostructured product reduces the porosity values and increases the mechanical resistance more than the ethyl silicate while the reduction of water vapor permeability is lower. Also, the addition of an organosiloxane (PDMS) to achieve hydrophobic properties has been studied, showing that the mesoporous gel obtained increases the pores size, enhancing the surfactant elimination and creating a dual roughness scale (micro and nano), improving resistance and the surface hydrophobic characteristics, besides increasing its flexibility, thus preventing cracking. Besides, by preventing cracking, water penetration into the stone porous structure is also avoided [23,24].

Although the literature contains many papers describing the use of silanes on stone, there are few that attempt to come to grips with the underlying chemistry or the associated sol-gel technology [25]. Nanostructured materials such as microemulsions, micellar solutions, dispersions of alkaline nanoparticles and chemical gels, can be used to effectively counteract the degradation processes without altering the physico–chemical properties of the treated works of art, and to minimize or completely avoid drawbacks [26].

The goal of this research is to assess the consolidation effect of a very common Mediterranean calcarenite stone with the nowadays most frequently used conventional ethyl silicate products and the most innovative consolidating materials based on nanostructured and nanoparticles. The relative humidity of the consolidation environment (very humid and dry) was attended to know its influence on the physical properties achieved by the stone after consolidation and hence in the efficacy of the consolidation process.