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K/Na-silicate, ethyl-silicate and silane nano-molecular treatments in the restoration of high porous limestone

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Abstract
Carbonate sedimentary rocks (*i.e.*, limestones) have been frequently used in historical times due to easy availability and workability. These latter depend primarily by petrophysical characteristics (porosity, bulk density) that influence the mechanical strength. However, the limestones with high porosity (>30%) and a poorly cemented carbonate-matrix show chemical alteration (i.e., dissolution) and physical decay (*e.g.*, decohesion).
In this work it was taken as case study a biomicritic limestone belonging to the carbonatic miocenic series (lower Tortonian) of Cagliari (southern-Sardinia, Italy). This limestone has a low-medium cementing matrix containing hygroscopic clay and sea-salt phases, which make the rock degradable. To limit the decay it can intervene with consolidating products (K-Na-silicate, ethyl-silicate) and protective-chemicals (silane nano-molecular gel-coat) to reduce the porosity and permeability to the liquid aqueous phase. Results highlight an increase of strength after consolidation and a decrease of gas-permeability after protection-treatment, maintaining in both cases a good permeability to the vapor-phase.

Keywords: consolidating, protective, porosity, gas-permeability

1. Introduction

Sedimentary rocks, particularly those carbonate type (e.g., limestone, sandstone, etc.), are widely used in the construction of historical building of Sardinia island as well as in many Italian monuments (Matera, Central Basilicata; Lecce, Southern Puglia) or other Mediterranean countries (Malta and Gozo Islands, Balearic Islands). Carbonate rocks of Miocene, mainly limestone, outcropping around Cagliari (Southern Sardinia, Italy) are frequently used in civil and historical architecture of the city in all periods, from Nuragic to Phoenician-Punic, to Roman to medieval [Columbu and Verdiani, 2014; Macciotta et al., 2001]. Miocenic series consist mainly (from the bottom in the stratigraphic sequence) of the following three facies; clays ("Argille del Fangario" Auct), sandstones ("Arenarie di Pirri" Auct) and limestones ("Calcari di Cagliari", Auct): marly limestone ("Pietra Cantone" Auct), biocalcarenites ("Tramezzario" Auct) and the biohermal limestone ("Pietra forte" Auct) [AA.VV., 2005; Barroccu et al., 1981; Cherchi, 1971]. Pietra Cantone stone is a marly limestone characterized by medium-low cementing degree, high porosity and easy workability. Given the wide availability in the territory of Cagliari, this limestone has been widely used to the historical building. For that reason derives its name where the word "Cantone" means ashlar [Lovisato, 1901]. Its easy workability is due to its petrophysical characteristic: poor internal cohesion between the crystal granules and the carbonate matrix. Such stone, once used in the masonry, it is not protected by plaster, in the presence of humidity or circulating aqueous solutions, show frequently problems of chemical-physical decay. These latter are due also to varying percentages of hygroscopic clay minerals and sea salts, which make the rock easily degradable with decrease of mechanical strength. When limestone is used in structural elements of monuments (e.g., ashlar in the wall, column, jambs, etc.), the decay can lead to formation of serious static-structural criticality in the buildings, as a strong retreat of the vertical profile of the façade or detachment of portions of material from decorative working parts, due to exfoliation and flaking processes. To prevent the decay of these carbonate rocks used in the monuments around the world are numerous the efforts to laboratory experimentation in regard to their protection and surface consolidation. They differ both in the products used for that application methods. Furthermore, due to the multiplicity of chemical, physical and mineralogical-petrographic characteristics of these lithologies, microclimatic conditions and alteration degree of the artefacts, the conservative techniques, however, are identified in each case. Among the products used are very common silicon-based on polymeric materials applied as monomers (e.g., ethyl silicate), or as oligomers or polymers or nano-dispersions (e.g., nano-silica), vinyl polymers (e.g., acrylic resins, fluoro-elastomeres) or inorganic (nano-limes, oxalates). In the scientific literature, several authors have dealt in various ways from a geological, geomechanical and engineering point of view the limestone of the Cagliari area [Barrocu et al., 1981; Carmignani et al., 1991] or similar lithologies. Through non-destructive analytical methods (seismic surveys, ultrasonic and termographic methods; e.g., Christaras et al. [2015] and mechanical tests in laboratory and in situ [Barrocu et al., 1981]. Other authors have studied the relationship between the microstructural properties and macroscopic performance of the stone [Price, 1996]. Atzeni et al. [1991, 2006] explore the mechanisms of water induced microstructural weakening in a porous limestone under water "static" presence and flow conditions using the Pietra Cantone of Cagliari as experimental model.

The present work aims to evaluate the efficacy of two kinds consolidation chemicals (based on K-Na-silicates and ethyl silicate) and a protective product (nano-molecular silane monomer water repellent) to use for restoration works of the "Pietra Cantone" limestone of the monuments. The choice of impregnating treatments depends on nature and cohesion of the surfaces. In fact information about this lithology and degradation phenomena were provided. To achieve these purposes the present work identifies a theoretical and technical methodological protocol for assessing characterization of materials, consolidation and protection chemicals. Also critical aspects will be identified and they will be discussed interpreting the results because the application methods and dosage of chemicals should be done consciously, through a careful study of interaction of products with stone in function of time. These products are considered compatible in chemical and physical terms with the limestone carbonate matrix [Escalante, 2000]. To evaluate the chemical compatibility with the material and the performance of selected products, a mechanical comparison and physical properties (i.e., strength to point load test, uniaxial compression, flexural resistance, water absorption, porosity, gas-permeability) before and after the chemical treatment of the limestone samples from monument has been done. The relevance concerns ability of individual technics to integrate during measurements and interpretation of acquired results. Through this methodological approach the importance of applied petrography is highlighted as a support to experimental chemistry for restoration both in construction and in cultural heritage. The limestone samples on which were carried out laboratory experimental treatments belong to the walls of an ancient building (XIV cent. AD) modified over time to become in the XVIII century an important tobacco factory of Italian "Monopolio di Stato" located in Cagliari city (Fig. 1).

Fig. 1- View of Tobacco factory masonry of "Monopolio di Stato" (Cagliari)

2. Material and methods

2.1 Sampling and geomaterials

The sample material was collocated from masonry-walls of tobacco factory during its restoration (Fig. 2). Three coarse fragments signed with MSA, MSB, MSC respectively of different limestone ashlars were sampled, compatibly with the limits imposed by local Superintendence of Cultural Heritage which suggests sampling methods minimally invasive or destructive, in order to don't affect the structural balance of the building and preserve the itself original characteristics. It is tried to taken rock fragments in order to verify the variability of compositional characteristics.

In laboratory, of each sample was cut into: 30 specimens with size 15*15*15 mm on which determinate the physical properties (real and bulk density; real volume; solid phase volume and density; total porosity, open porosity and closed porosity to water and helium (Helium Ultrapycnometer 1000, Quantachrome Instruments); water absorption with imbibition coefficient and saturation index. Vapour permeability was determined on samples with size of 50*50*10 mm according to NORMAL 21/85 (1985).

Petrographic and mineralogical characteristics were determined by optical polarized light microscopy (OM, Leitz Wetzlar) on polished thin section. On powder samples carried out the qualitative mineralogical characterization of crystalline phases through X-ray diffraction (XRD) analysis and scanning electron microscopy investigation (SEM).

Fig. 2- Macro-photograph of original Pietra Cantone limestone ashlars taken from monument of tobacco factory during its restoration

To determine the mechanical properties before and after the chemical treatments, of each ashlar sampled were cut: cubic specimens with size 50*50*50 mm for the uniaxial compression (UNI EN 1926/2007) using Controls Instrument 50-c40 model; prismatic specimens with size 12*50*20 mm for the flexion test according to UNI EN 12372 (2007); cubic specimens 20*20*20 mm for Point load test (by D550 Controls instrument) according to ISRM (1972, 1985).

Ultrasonic velocity testing has been effectuated on cubic specimens with size 50*50*50 mm according to the standard UNI EN 12504-4(2005) and ASTM C597 09/2009 (Ultrasound Controls 58-E4800). The values of ultrasonic wave time travel were determined with the indirect method before treatment and after 24h, 7 days and 24 days.

2.2. Chemical treatment methods

Two different consolidant products (CM and FB) and a protective chemical (NG) are used. All the specimens, before treatment, have been cleaned superficially through the removal of the fats resulting from the sawing operation and they were placed in the stove at 60°C for 72 hours. The consolidants were applied by immersion of the specimens in fiberglass becker (Fig. 3) for a duration of 24 hours and exposed, finally, at an ambient temperature between 20-25°C and relative humidity of 40-50% sheltered from sunlight ensuring complete and homogeneous absorption by the stone, saturating without distinct all pores. In practice it may seems unattainable, but the restorers apply the product by spraiyng in several coats spaced from each other of a few hours with a pressure of 0,5 bar or by controlled injection anchors with a special sock. The admissible grouting pressure has to be controlled according to the state of masonry (0,5 bar). The injection is done gradually until the anchor is fully injected ensuring complete saturation of the masonry.
The nano-molecular hydrophobic was smeared with paint brush (Fig. 4).

Fig. 3- Chemical treatment by immersion of cubic and prismatic limestone specimens

Consolidating CM (called "Mineral consolidant") it’s a concentrated impregnating product of silicates, mainly potassium and sodium silicates in greater quantities in hydro-alcoholic dilution. This solution forms chemical reaction with the salts of the stone and with calcium hydroxides forming Ca/Na/K-carbonates stabilized binders and amorphous silica.

Fig. 4- Cubic limestone specimen with edge 5 cm treated with nano-gel

Hydrolysis of alkaline elements leads to the formation of hydroxide, which are conveyed during the evaporation of the solvent that cause efflorescence in the surface of the stone. This process does not affect negative effect because the alkaline elements of CM dilution renewing stone matrix. The silica has strong capabilities consolidating and aggregating, and Si-O underlying the silica derivatives is very stable [Beninatto et al., 2007]. The formulation makes CM consolidant particularity pervasive in the wall.
Ethyl silicate hardener FB (called "Indur") contains the 70% of ethyl silicate in alcoholic fluid dilution. The product precipitates by hydrolysis (Fig. 5) following a reaction with atmospheric moisture that acts as catalyst, forming ethyl alcohol as a secondary product. Products penetrate as liquid phase, after about two weeks silica goes to viscose phase according to the sol-gel process [Sponchia, 2011]. Consolidation is effectively complete after about 3-4 weeks when the silica gel will complete its transition to the amorphous state forming also Si-O binders stabilized that fills the pore and the intergranular spaces. Hydroxyls linked to the impurities fraction in limestone (i.e., illite, montmorillonite; Fig. 5) have an important role because are sufficient to bind colloidal silica to carbonate matrix [Mameli, 2012].
Water repellent protective (NG) used in this research is a nano-molecular gel based on

silane monomer in a concentration of 42-43 %. So it can dissolve in polar solvent such alcohols. The hydrolysis reaction produces alcohol as a by-product, which rapidly evaporates and promotes silane condensation.
This process comprises a three dimensional molecular network which provides water protection to the porous substrate of the stone [Larry et al., 1996].

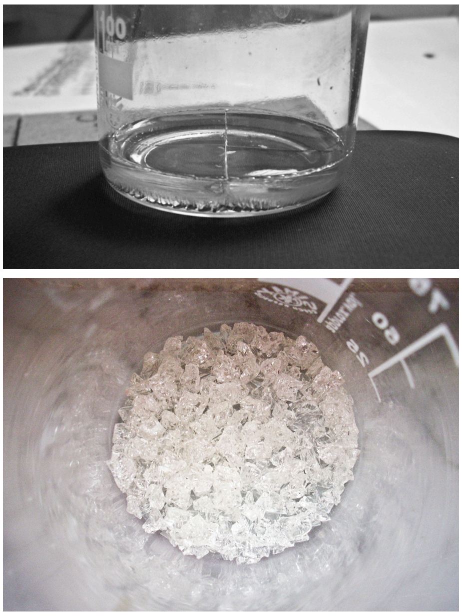

Fig. 5- (photo above) first nucleation of amorphous SiO_2 phases of ethyl silicate consolidating, (photo down) amorphous SiO_2 solid phases after 60 days from the beginning of consolidation

3. Result and discussion

3.1. Petrographical and mineralogical characteristics of Pietra Cantone limestone

According to Folk [1959] and Dunham [1962] classification the three samples of Pietra Cantone can be defined as biomicritic limestone and as wackestone, respectively. However, on the basis of microscopic observation and given the environment of deposition conditions, it is preferable to define them as marly limestones poorly cemented, with mainly muddy microcrystalline matrix consisting of a component substantially calcitic (about 90%vol. of total granules) and subordinately silicatic (< 10%) and variable presence of bioclastic component (30% mostly Globigerinidae foraminifera) and fragments of varius shell.
XRD analysis confirm the main presence of calcite, quartz, occasionally phyllosilicate (i.e., illite group) and occasionally gypsum as results of sulfation of carbonate matrix.
To deepen knowledge on the composition and microstructural aspects of Pietra Cantone, SEM analysis on external surface of untreated samples show a crystalline micrometric structure consisting mainly of granules of calcite (>85%), quartz, K-feldspar, biotite, illite and rare apatite crystals, bioclastic fragments (20-30 microns) and mixed chlorides of Ca/K/Na are present, dangerous fact for the physical and chemical decay of the stone with progressive dissolution of the carbonate matrix and (partially) of calcite microcrystals.

3.2. Physical properties of Pietra Cantone limestone and protective efficacy

Porosimetric analysis with helium picnometry on the MSA, MSB, MSC Pietra Cantone samples studied has revealed variable values of total porosity with frequent range about 28-34 % vol%. Closed porosity is always < 1%.

SEM analysis highlight that the pores vary frequently in the range of 5-50 μm but also >50 μm. Due to the presence of terrigenous clay minerals (i.e. phyllosilicates) and salts (e.g. gypsum, Na-carbonates, NaCl, etc.) this limestone is easily degradable at the presence of humidity that constitutes an even more dangerous factor for the chemical and physical decay of the limestone.

After chemical treatment with NG the same sample MSA, MSB, MSC show similar values of physical properties of total, He and closed porosity while chemical enables to limit the liquid phase permeability. In fact, water open porosity varies to 6-7% on untreated sample and 4-4,8 % on samples with NG protection. The imbibition coefficient show a significant decrease that varies from 3,2-3,7% on untreated samples to 1,9-2,5% with NG protection. As regards Saturation Index effectiveness is further highlighted by the range values of 18,6-20,4 % of untreated samples and 13-15% of protected samples. Permeability average values ranges from 0,45 g/m^2x24h in MSB, 0,56 g/m^2x24h in MSA and 0,76 g/m^2x24h in MSC. It highlights that, aside from absolute values but evaluating the overall trend, it be considered that the nanogel protective facilitates the passage of the aqueous vapour phase.

3.3. Mechanical characteristics of Pietra Cantone limestone and consolidating efficacy

The efficacy of two consolidation treatments (CM, FB) in Pietra Cantone limestone was made by a comparision before and after the treatment following physical properties: longitudinal wave ultrasonic velocity (Vp), resistance to puntching strength $Is_{(50)}$ (PLT), uniaxial compression (Rc) and flexion (Rf) strengths. The test results of Vp before and after the treatment (at 15 days) show a clear improvement of the compactness characteristic of specimens analysed (MSA, MSB MSC). Velocity was calculated on the direction of Z axis, that represents the main direction where occurs the compressive stress of lithostatic load; there is a fluctuating behaviour of velocity in function of drying time and type of chemical.

A validation of consolidation effectiveness was obtained comparing the mechanical tests results of the samples untreated and consolidated are shown in Table 1. The physical-mechanical tests have shown a clear increase of compactness and resistance to stress of flexural, compressive and PLT following treatment with consolidants CM and FB. The resistance values of compression increase considerably:

- in the case of the CM, the percentage increase vary from 39% in the rock types MSB to 67% in MSC;
- in the case of the product FB, the values vary from 91% in MSB to 151% in the MSC.

Sample		$Is_{(50)}$	Rf	Rc	Ultrasound Velocity on Z axis
		[N/mm^2]	[MPa]	[MPa]	[m/s]
MSA Untreated	mean	0.50	0.7	9.48	553.36
	st.dv.	0.26	0.14	0.20	
MSA CM	mean	1.13	1.1	14.44	1344.09
	st.dv.	0.22	0.31	0.46	
MSA FB	mean	1.79	1.3	23.08	2008.32
	st.dv.	0.12	0.23	0.78	
MSB Untreated	mean	0.70	0.7	9.21	652.29
	st.dv.	0.17	0.18	0.15	
MSB CM	mean	1.15	1.2	12.80	2.024.29
	st.dv.	0.16	0.18	0.43	
MSB FB	mean	1.66	0.8	17.55	1208.00
	st.dv.	0.20	0.28	0.26	
MSC Untreated	mean	1.28	0.6	7.40	919.12
	st.dv.	0.08	0.1	0.32	
MSC CM	mean	1.42	0.8	12.74	1392.76
	st.dv.	0.14	0.12	0.22	
MSC FB	mean	1.87	1.1	18.57	1415.00
	st.dv.	0.36	0.15	0.54	

Tab. 1- Physical and mechanical data of tests determined on untreated and treated specimens of Pietra Cantone limestone; st.dv. = standard deviation; $Is_{(50)}$ = Point Load Index; Rf = flexion strength; Rc = uniaxial compression strength

To deepen knowledge on the modes of absorption and adhesion of the chemical product to the limestone and the related microstructural aspect, SEM analysis on the external surfaces of the treated samples were made. In the sample treated with CM consolidating, besides the Na/K-silicates and amorphous silica, it is observed the presence on surface of NaOH agglomerate salts (as efflorescence) with elongated crystal, often according to a curvilinear trend. In the samples treated with FB consolidating it is observed the presence on surface of cracked chemical product (from 0,5 to 4 microns) that may be due also rapid evaporation of ethyl alcohol and/or thermal differential expansion between the amorphous silica and the crystalline substrate. The spot multispectral chemical analysis shows a silica-based compound. In the sample treated with NG protective it is observe the water repellent silane condensed in porous network bonded to the carbonate matrix.

4. Conclusions

Results of physical, mechanical and petrophysical analysis before and after treatment with chemical products has permitted to highlight chemical compatibility and effective efficacy of protective water repellent and consolidating.

The protective gel based on silane monomer is a good solution to treat limestone. This product enables to limit the permeability to liquid water phase, as demonstrated by a clear lowering of the open porosity to water, the absorption coefficient and of the saturation, while at the same time allows an almost unchanged permeability to the vapour phase.

The physico-mechanical tests have shown a clear increase of compactness and resistance to stress of flexural, compressive and PLT following treatment with consolidating products CM up to 67% and more in FB up to 151%. The resistance values of compression increase considerably. The results highlight a better consolidation of degraded materials characterized by high porosity and low cohesion degree (MSB and MSC). The ultrasonic velocity confirms the excellent quality as consolidating of both products, in particular the product FB.

The flexion test clearly highlighted the qualitative improvement of compactness and resistances. In the case of product CM, the increases vary up to 63%; in the case of FB, the values reach an increase of 102%.

Definition of the mineralogical-petrographic features (by OM and XRD), chemical SEM-EDS and physical analysis were necessary and extremely important to verify compatibility between limestone and chemicals and to analyse the critical aspects, because modes of absorption and adhesion of the chemical products to the microstructure of rock affect the restoration efficacy and durability. Hydrolis processes of alkaline element and solvent evaporation in the use CM "Mineral consolidant" may produce NaOH-efflorescence in some surface portion of stone. Therefore, prior to application of the CM, masonry desalination is recommended before the use of the CM chemical or efflorescence later can be easily removed with a low-pressure vaporizer. It’s advisable after a few days to apply a plaster based on natural hydraulic lime that not affect the consolidation process of CM because this plaster has the same breathability of the stone and it does not hinder the solvent evaporation process. For the reasons use of CM chemical is considered suitable for the consolidation of civil structures masonry also because the formulation costs are less onerous than the "Indur" FB (less about 35%).

As regards to *ethyl silicate* FB has been demonstrated that the presence of the illite or other secondary impurities with hydroxyl groups is sufficient to bind colloidal silica to carbonate matrix forming a compact network able to withstand high mechanical strength to the Pietra Cantone limestone. Presence of efflorescence is not detected in any samples. Given the greater effectiveness and high production costs this chemical is especially suitable to consolidate masonry of architectural structures and monumental value with stone face-to-view.

The use of nano-gel as waterproof protective has proved effective in the preventive conservative treatment of limestones characterized by high decay with high porosity (>30%), in so far as does not allow the passage and absorption of liquid aqueous phases (rainwater and condensation), leaving an unchanged breathability to the gaseous phase. The results showed that in this case even a slight increase of the mechanical resistance to work of such protective treatment.

After drying of the walls and the effective consolidation and protection change colour have not been verified.

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