12th International Congress on the Deterioration and Conservation of Stone
Columbia University, New York, 2012

THE NEAPOLITAN YELLOW TUFF AND THE VICENZA STONE: EXPERIMENTAL INVESTIGATIONS ABOUT EFFECTIVENESS OF ANTISWELLING TREATMENT.

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Abstract

In this study, two relevant geomaterials, traditionally employed as building stones, the Neapolitan Yellow Tuff (a volcanoclastic rock, hereafter NYT) and the Vicenza Stone (a porous sedimentary rock, hereafter VS), were consolidated under laboratory conditions. Although with different genesis and composition, the two stones display similar pore radii distribution and this allows to better evaluate the mechanisms of stone consolidation.

Goal of this research is to test the performance of a consolidation with Ethylsilicate based product (PRC110, hereafter ES) on these stone materials previously treated with an antiswelling commercial products (Antihygro, hereafter AH); the use of AH is intended to reduce the swelling ability of some minerals contained in NYT and VS.

Keywords: Neapolitan Yellow Tuff, Vicenza Stone, consolidation, durability, antiswelling.

1. Introduction

The use of the stone as building and decoration material has ancient origin and Italy offers several examples of stone used over the centuries in sculpture, decoration, road paving, etc.

Building stone are often affected by deterioration caused by weathering which sometimes causes irreparable damage.

During the past intervention, replacing damaged blocks was a cheap solution, but nowadays it's almost difficult to due to the closure of many quarries.

In the recent years many efforts have been made to search products able to consolidate and stabilize weathered material and to reduce stone decay, protecting it from the causes of degradation.

The choice of a conservative intervention is a very risky phase that requires a thorough knowledge of the stone.

In this study a Campanian tuff, NYT and a biodetrital carbonate, VS were treated with conservative products, an ethyl silicate and an antiswelling protective, to evaluate their effectiveness against weathering mechanism.

NYT was used as a building material since ancient times because of its peculiar colour, light weight, easy workability and good insulating property.

VS was used as building stone mostly in Vicenza, Verona and Padova, with architectural and decorative function. Both the stones display high porosity that makes them extremely vulnerable to deterioration caused by weathering.

The effectiveness of conservative treatments was evaluated by mineralogical and physical-mechanical investigation and by ageing test.

2. Materials

NYT is the most important volcanic product in the Neapolitan area, linked to a phreatomagmatic eruption in the area of Campi Flegrei (15,000 y.b.p; Deino et al., 2004). It is characterized by an altered ashy matrix containing zeolites and very subordinate clay minerals (smectite); the most abundant zeolitic phase is phillipsite, along with chabazite and analcime in minor amounts (de' Gennaro et al., 2000). Primary phenocrysts are represented by sanidine, pyroxene, mica, plagioclase and magnetite (de' Gennaro & Langella, 1996; de' Gennaro et al., 2000). Its chemical composition ranges from trachyte and alkali-trachyte to phonolite (Scarpati et al., 1993; Orsi et al., 1995).

The VS is a biodetrital carbonate formed at back-reef in the tidal channels during Oligocene (33M y.b.p.; Mietto, 1988).

It is a limestone characterized by high calcium carbonate content (90-95 per cent) and low content of both silica and clay components and with non-negligible percentage of aluminum oxides and iron (Marchesini et al., 1972; Cattaneo et al., 1976).

The main biogenic components are foraminifera such as Amphistegine and Lepidocicline, Briozoi, red algae Melobesoidea, corallinae algae.

Frequently, in the case of monumental buildings, the ornamental stones were used *facciavista* and this makes them more sensitive to weathering processes. The basic agent of this phenomena is mainly represented by water that plays a decisive role in the weathering of stone surface: its action is manifested both directly (through hydrolysis processes in silicates and dissolution in carbonates), and indirectly (through processes of hydration-dehydration,freeze-thaw cycles, crystallization of salts).

The most frequent weathering typologies of NYT are: alveolization, mainly due to detachment of particles such as lithic clasts or zeolitized pumices; scaling and exfoliation both due to the combined action of damp waters and subsequent recrystallization of soluble salts; disaggregation due to infiltration of water and the consequent dissolution of the constituent phases of the stone; patinæ, stains, efflorescences due to the evaporation of damp waters and consequent deposition of soluble salts on stone surface.

It should be noted that most of these forms such as scaling and exfoliation are promoted by the presence of minerals with swelling properties such as zeolites and/or clay.

The weathering forms visible on the surfaces in VS are mainly due to dissolution and pulverization processes and biological activity; humidity traces, and black crusts are often present.

2.1 Products

Two commercial products have been used both with NYT and VS: a silicate-based consolidant (ES) and a protective having antiswelling properties (AH), which was applied before ethyl-silicate (table 1)

Table 1. Characteristics of tested products

Product	Company	Composition	Abbreviation	Density (gr/cc)
PRC110	Fila	Etylsilicate	ES	1.060
Antihygro	Remmers	Tetramethylenediammonium dichloride	AH	1.000

ES is a one component-system based on organic compound of silicon, produced by Fila Industria Chimica Spa (S. Martino di Lupari – Padova). The consolidation effect is primary due to deep penetration into the pores and furthermore its ability to react with the silicate matrix (as in the case NYT).

AH is a tetramethylenediammonium dichloride in aqueous solution. Its property is to reduce the hygroscopic swelling of stone, leaving unchanged their physical-mechanical characteristics.

3. Methods

The NYT was collected from Chiaiano quarry, in the northwestern part of Naples.

The VS was quarried in Nanto (VI), located on the Colli Berici and was provided to us by Marmi Sgambaro SNC company (S. Martino dei Lupari-PD).

Consolidation has been achieved by total immersion. The specimens were divided into the following test groups: untreated, treated with consolidant (ES) and treated with antihygro and consolidant (AES). The samples treated with AH were air-dried for one week, those treated with ES for three weeks (in agreement with its polymerization time).

Laboratory tests (mineralogical and petrographic analyses, physic-mechanical determinations and ageing test) were carried out before and after application of each treatment according to European-suggested standards (UNI EN, NORMAL).

3.1 Mineralogical investigation

Mineralogical composition was carried out by X-ray powder diffraction (XRPD - Panalytical X'Pert Pro; CuKα radiation, 40kV, 40mA, 4-80º 2θ scanning interval, 0.017º equivalent step size, 60 sec per ste equivalent counting time, RTMS X'Celerator detector), optical microscopy (Leica Wild MZ 8) and SEM observations (Jeol JSM 5310 Oxford Inca- CISAG, Federico II University of Naples).

Quantitative mineralogical analyses were performed by XRPD using "Reference Intensity Ratio" (RIR - Chipera e Bish, 1995) technique. Powders with grain size less than 10 μm were obtained using a McCrone micronizer mill; such a particle size allows several problems to be overcome, such as: particle statistics, primary extinction, microadsorption and preferred orientation. (Klug & Alexander, 1974)

The EDX analysis (FEI Quanta 200 scanning electron microscope) were performed to evaluate the penetration depth of consolidating products into the stone by measuring the concentration of silicon in untreated and treated samples and were carried out at the ICIS Istituto di Chimica Inorganica delle Superfici di Padova.

3.2 Physical-mechanical investigation

The physical-mechanical investigation was carried out by swelling test, thermal expansion and ageing tests.

The influence of water on the behavior of both untreated and treated stones was evaluated by swelling tests following the procedures suggested by Nascimento et al. (1968); particularly the swelling strain was measured on cubic specimens (side of 5 cm) using an apparatus suitably realized by Lonos Test S.r.l. (Monza) and able to measure a volumetric swelling strain by five digital micrometer arranged along the three axes (x,y,z).

The thermal beahviour was carried out on prismatic specimens (25 cm x 5 cm x 2,5 cm); according to the NORMAL UNI EN 14581 the tests were performed using a mechanical device which allows to record variation in length of specimen with increasing temperature.

Ageing tests included salt crystallization tests, freeze-thaw and salt spray test. All these tests were performed according to standard procedures (UNI EN, 12370 UNI EN 12371 and UNI EN 14147 respectively).The tests were chosen taking into account the weather conditions of the areas where the two stones are used. In order to assess the change of physical-mechanical features, weight, open porosity, ultrasonic wave and UCS were measured before and after treatment.

Open porosity was calculated by means of apparent and real volume with an He pycnometer (Micromeritics Multivolume Pycnometer 1305) on cylindrical specimens.
Uniaxial Compressive Strength test were performed according to UNI EN 1926 (Controls C5600), with maximum load of 3000 kN and a load constant rate of 1 ± 0.5 MPa).

Freeze-thaw cycles were carried with a Binder MK 53 climatic chamber. Saturated specimens were placed in climatic chamber for 6 hours at a temperature ranging from 20º to -12º C and then immersed in water at room temperature for 6 hours.
Salt crystallization cycles were carried out by immersing cubic specimens (side 4 cm) in a saturated solution of sodium sulfate dechaydrate for 2 hours. Specimens were then dried in oven at 105 ± 5 ° C at least 16 hours, cooled for about 2 hours and re-immersed in a fresh solution. The cycle is repeated for 15 times.
Salt spray test was carried out at the Fila Industria Chimica Spa (S. Martino di Lupari - Padova). It was performed on cubic specimens (side 5 cm) by an ERICHSEN Corrotherm 610 climatic chamber (400 litres), capable to alternate cycles of treatment with salt spray (sodium chloride) and drying. The test consists of 60 cycles.

4. Results and discussion

NYT is characterized by altered ashy matrix containing zeolites and subordinate clay minerals; the authigenic phase are phillipsite (55 per cent), chabazite (3 per cent), analcime (4 per cent) and smectite (4 per cent).The pyrogenic minerals are represented by sanidine (23 per cent), pyroxene (2 per cent), mica (traces), hydrated iron oxides (traces). The volcanic glass and/or the amorphous component is roughly 11 per cent.

The diffraction analysis performed on the VS show calcite as prevailing phase (98 per cent) and subordinately quartz (1 per cent), clay mineral (1 per cent) and iron oxides (traces).

The penetration capability of AH into the pores is more difficult to detect by SEM or EDS techniques, mainly due to low chlorine content. On the contrary the effectiveness of ES treatment was highlighted by means of EDS analyses of the Si concentration along the cross section of treated and untreated specimens (side 5 cm; figure 1). First of all, it is notable the deep penetration of the ES in the entire section of the specimens for both lithotypes. Furthermore the pretreatment with AH does not seem to influence the ES penetration except for NYT (figure 1, on the left) in which is clearly observed a lowering of the silica percentage, in the range from about 200 to 300 mm, close to the untreated samples.

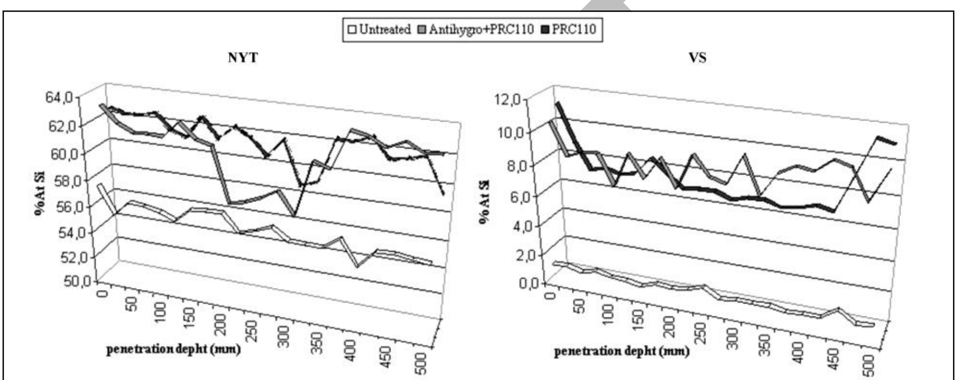

Figure 1 Profiles of the Si concentration (in atomic percent) along the cross section of NYT (left) and VS (right) specimens both untreated and treated.

Expansion or shrinkage as a result of water imbibition or temperature variations play an important role in the stone deterioration especially for tuffs (Steindlberger, 2004). This parameter are strongly influenced by the mineralogical composition of the stone and their evaluation can provide significant informations in all those contexts characterized by constant presence of water or major climatic excursions, both daily and annual. The expansion coefficient is negligible when the stone can expand; on the contrary, when even expansion is prevented, tensions that are created within the rock can go beyond the value of resistance to compression, or be likely to cause flexing and bending of the buildings (Primavori, 1999).

Changes in the dimension of the specimens due to rock swelling after water immersion, were measured (table 2). The hygric expansion of the untreated stone mainly depends on the content of phases with swelling capability, such as clay and zeolites. This explain the greater tendency to dilation of the NYT compared to VS.

A strong decrease of expansion (more than 60 per cent) was recorded for NYT after pretreatment with AH (figure 2). A strong decrease of expansion (more than 60 per cent) was recorded for NYT after pretreatment with AH (figure 2).

Table 2. Comparison of some physical-mechanic parameters for NYT and VS before and after conservative treatments (means value).

	NYT			**VS**		
	Untreated	AES	ES	Untreated	AES	ES
Samples number	5	5	5	5	5	5
Amount of applied product (%)	—	20	18	—	5	6
Hygric dilation (%)	0.65	0.20	0.42	0.033	0.086	0.086
Linear coefficient of thermal dilatation (10^{-6} mm/mm °C)	-25.50	-11.73	-11.35	3.10	1.98	2.02

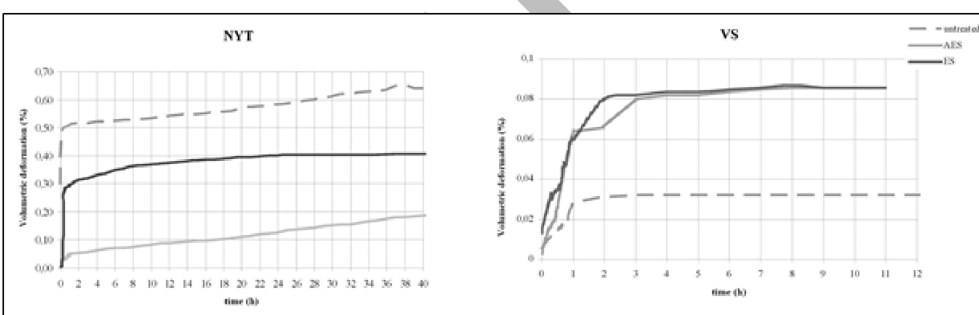

Figure 2 Volumetric dilatation of NYT and VS, both untreated and treated.

The NYT thermal behavior with increasing of temperature is characterised, in accordance with literature (Marino et al., 1991; Colella et al., 2009), by a dimensional shrinkage due to dehydration of the zeolitic cement (table 2).

The linear coefficient of thermal expansion of untreated NYT is about -26 10^{-6}mm/mm ºC; the consolidated samples show a lower contraction, which is about -12 10^{-6}mm/mm ºC and -11 10^{-6}mm/mm ºC, for AES and ES samples, respectively.

In contrast, the VS shows an average coefficient of thermal expansion of 3 10^{-6}mm/mm ºC; This dilation is related to the response of the calcite to the increase in temperature, the crystal shrinks in one direction and expands in the direction orthogonal to the previous (Rota Rossi-Doria, 1987). Both AES and ES effectively contrast VS dilation with lower values by 33 per cent (table 2).

In order to evaluate durability of consolidated stones is necessary to carry out test able to reproduce the environmental condition in which the stone is used.

Therefore stones have been tested by ageing test such as salt crystallization, freeze-thaw cycles and salt spray.

The variation of the physical-mechanical properties was reported in table 3.

Salt crystallization is one of the most powerful weathering agents for the stone. This test resulted very aggressive for NYT for both untreated and consolidated samples (AES and ES). This behavior is probably due to decrease in pore spaces that resulted in a more effective pressure of crystallization. Consolidated samples are broken down completely before the end of test with the same times of the untreated (table 3).

Different behavior is observed for the VS: salt crystallization cause a considerable loss of material for the untreated samples. On the contrary, all consolidated samples show good resistance to weathering induced by repeated salt crystallization cycles, as evidenced by the low weight loss (table 3).

Table 3 Variation of the main petrophysical properties in NYT and VS (untreated and treated) after ageing tests.

		NYT			VS		
%		**sc**	**ft**	**ss**	**sc**	**ft**	**ss**
weight loss	**Unt**	disag.	2	2	73	6	1
	AES	disag.	4	4	1	1	2
	ES	disag	disag.	4	1	1	2
compressive strength	**Unt**		disag.			not mes.	
	AES		-17			0,5	
	ES		disag			-7	
porosity	**Unt**		disag	4		3	2
	AES		disag	13		4	13
	ES		disag	17		9	30

sc= salt crystallization; ft= freeze-thaw cycle; ss= salt spray; disag=disaggregated; not mes= not measurable.

The behavior of tuff during freeze-thaw cycles is changed by pretreatment with AH. The unconsolidated NYT shows a strong degradation with intense fracturation in the early cycles. The stronger degradation is showed by NYT treated with ES: in this case, in fact, the freeze-thaw cycles lead up to disaggregation before the end of the test. NYT treated with AES, on the contrary, does not show, except for a single test specimen, fractures at end of cycles.

The behavior of NYT to the frost action is closely related to the kinetics of water absorption: fast saturation of porous system causes a more effective pressure into the stone when water pass to solid state.

As regards VS, freeze-thaw cycles mainly act on some portions, brownish in color, clearly distinguishable and well localized.

The EDS analysis performed on these portions indicate the presence in addition of calcite, quartz, iron oxides and a micaceous component.

As a result of water absorption this portions swell creating pressure within stone. This phenomenon leads to physical degradation with loss of material due to pulverization.

The treated samples (both with AES and ES) do not show any weathering forms as confirmed by negligible weight loss (1 per cent)

Finally to evaluate the resistance to weathering that affected the building stone, in case of aggressive atmosphere, such as those typical of coastal areas, samples have been exposed to salt spray chamber.

Salt spray test preserved the original shape of the specimens both for the NYT and VS, as shown by the slight loss in weight (table 3).

As general remarks ageing tests produced an increase of total porosity and a reduction of the compressive strength either in untreated as treated stones; in other words, the durability was considerably reduced (Winkler, 1997; Goudie, 1999) and this is probably true for NYT, regardless of treatment method.

Moreover, alteration mechanism such as salt crystallization and freeze-thaw resulted more aggressive in stones with a high percentage of mesopores (r <1 μm; Rossi Manaresi, 1976).

5. Conclusions

The collected data represent a contribution to understanding of material behavior after conservative treatments in conditions close to those in which material will be used as building materials.

The choice of NYT and VS, silicatic and carbonatic in composition, respectively, allows to evaluating how the different nature of constituents influence the consolidation mechanisms.

Behaviour of NYT and VS during the thermal stress is affected by consolidation especially when the antiswelling is applied.

The consolidation with ethylsilicate showed poor compatibility with the NYT; by contrast, the consolidation was effective for VS especially in terms of durability.

A pretreatment with antiswelling was very effective for NYT, due to its high percentage of expanding phases. The VS did not appear to be influenced by this specific treatment.

The results indicate that the consolidation treatments for the NYT need a new approach. In this light, the good petrophysical properties shown by the TGVT (Tufo Giallo della Via Tiberina; PRIN 2008-2011), probably due to the presence of a calcitic cement, suggest that the future use of inorganic products (possibly inducing the formation of a similar cement) could improve the resistance to degradation of zeolitized lithotypes.

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