

EVALUATION OF PETROPHYSICAL PARAMETERS OF THE NEAPOLITAN YELLOW TUFF AND THE VICENZA STONE: EXPERIMENTAL INVESTIGATION ON CONSERVATION OF MACROPOROUS BUILDING STONES

CLAUDIA DI BENEDETTO

Dipartimento di Scienze della Terra, Università "Federico II" di Napoli, Via Mezzocannone 8, 80134 Napoli, Italy

INTRODUCTION

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 the materials from the causes of degradation.

In this study, two important geomaterials, traditionally employed as building stones, the Neapolitan Yellow Tuff (a volcanoclastic rock; NYT) and the Vicenza Stone (a porous sedimentary rock; 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 difference between the performance of a consolidation with ethyl silicate-based product (PRC110) on these building stones, also after a previous treatment with an antishrinkage commercial product (Antihydro), the latter aimed at reducing the swelling capacity of some minerals contained in VS and NYT.

MATERIALS AND METHOD

The 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 ash matrix containing zeolites and very subordinate clay minerals (smectite); the most abundant zeolitic mineral is phillipsite, along with minor amounts of chabazite and analcime (de' Gennaro *et al.*, 2000). Primary phenocrysts are represented by alkali feldspar, pyroxene, biotite, plagioclase, and magnetite (de' Gennaro & Langella, 1996; de' Gennaro *et al.*, 2000). The chemical composition of NYT ranges from trachyte and alkali-trachyte to phonolite (Scarpato *et al.*, 1993; Orsi *et al.*, 1995).

The NYT has been used as a building material since ancient times because of its peculiar colour, light weight, easy workability, and good insulating property. However, the abundant presence of zeolites (> 50 wt.%) and the high open porosity, ranging from 40 to more than 60%, make it extremely vulnerable to deterioration caused by weathering.

In this study NYT was sampled at Chiaiano quarry, in the north-western part of Naples.

The VS is a biogenic carbonate formed at back-reef in the tidal channels during Oligocene (33 My. B.P.; Mietto, 1988). The main biogenic components are foraminifera (such as *Amphistegina* and *Lepidocyclina*), Briozae, red algae *Melobesioidea*, and corallinae algae. The VS has been used as building stone mostly in Vicenza, Verona and Padova, with architectural and decorative function.

In this study the VS stone was quarried in Nanto (VI) located on the Colli Berici and was provided by the company Marmi Sgambaro SNC (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; ethylsilicate), and treated with Antihydro and consolidant (AES; Antihydro-Ethylsilicate).

Investigations were carried out before and after each treatment and included mineralogical and petrographic analyses (XRD, XRF, SEM), as well as physical and mechanical determinations (porosity, pore radii distribution, capillarity absorption, water absorption, ultrasonic wave velocity measurements, uniaxial compressive strength, colorimetric measurements).

Furthermore, the consolidated samples were subjected to ageing tests (such as freeze-thaw cycles, salt crystallization tests and salt spray) in order to evaluate and measure the effectiveness of consolidation and to study the changes of stone properties.

RESULTS AND DISCUSSION

SEM observation was performed to evaluate the distribution in the rock texture of the polymer. Ethylsilicate occludes the pore space, creating larger gel plates. Moreover a micro-fissure system within consolidant is observed (Fig. 1). This is due to the permanent hydrolysis of the ethylsilicate.

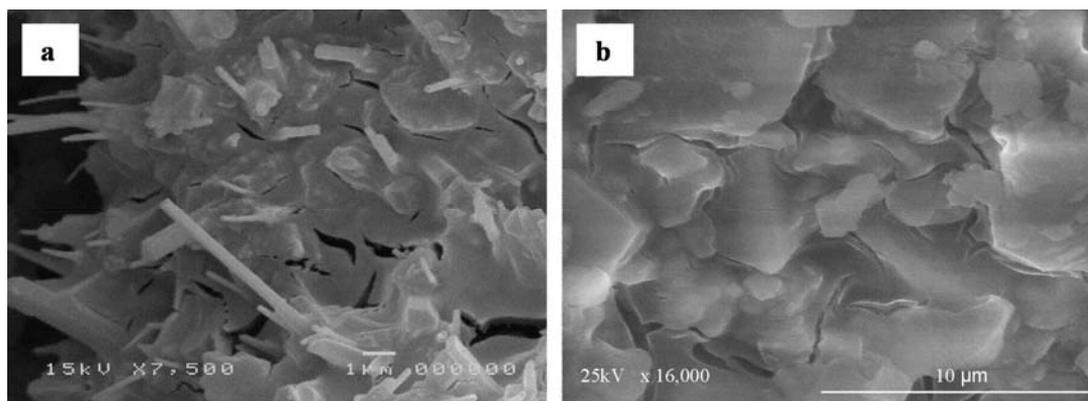


Fig 1 - SEM microphotographs of consolidant (ES) distribution on NYT (a) and VS (b) surface.

The penetration depth of the consolidant into the stone was evaluated by measuring the silicon concentration along cross sections both in untreated and treated samples. Consolidant distribution is almost superficial and strongly influenced by the stone porosity.

The consolidation induced changes in properties and behavior of stones and the main petrophysical variation after conservative treatments are given in Table 1.

The treatments strongly decreased the open porosity with, as a consequence, a lower water absorption by capillary uptake, both in NYT and VS; this could be attributed to the formation of a more tortuous path for water molecule penetration (Stück *et al.*, 2008). By contrast, treatments led to a reduction of the natural traspirability, as also confirmed by drying index (Table 1).

The pore size distribution was also modified by consolidation, especially for NYT, showing a significant decrease of mesopores. Both samples displayed an increase of the average pore radii, probably due to ethyl silicate hydrolysis, leading to the formation of secondary porosity in PRC110 (as shown by SEM observation).

In general the treatments defined an increase of the stone compactness: ultrasonic wave velocity and compressive strength also increased, likely due to the filling of pore space by consolidant.

The strong decrease of contraction (more than 50%) was recorded for NYT after pre-treatment with Antihydro, likely as a consequence of the occurrence in this rock type of clay and zeolites showing a good attitude to the swelling.

The intensity of stone hygryc dilatation mainly depends on the content of swelling phases. This explain the greater tendency to dilatation of the NYT compared to VS. Antihydro once again is very effective in reducing the hygroscopic swelling of NYT.

Treatments with PRC110 induced color change that caused darkening of samples, especially NYT ($\Delta E = 11$); on the whole, treatments with Antihydro did not produce significant chromatic change ($4 < \Delta E < 6$).

As far as, durability ageing tests were considered, such as salt crystallization, freeze-thaw cycles and salt spray; they had different effects for the two consolidated stones.

Results are reported in Table 2 and 3 for NYT and VS, respectively evidencing how these treatments were definitely effective for VS and not for NYT.

Table 1 - Comparison of 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
Bulk density (kg/m³)	971	1148	1178	1930	1985	2090
Specific gravity (kg/m³)	2277	2108	2082	2715	2620	2564
Open porosity (%)	53	46	43	29	24	18
Compactness degree (%)	43,45	54,47	56,53	71,20	75,75	81,49
Absorption coefficient (%)	44,80	35,99	36,02	10	7	8
Capillary absorption coefficient (g/m²)s^{-1/2}	313	3	2	127	2	2
P-wave velocity (m/s)	1794	2008	3732	3740	3773	3732
Uniaxial compressive strength (MPa)	3,31	6,36	7,72	22,54	31,72	34,97
Thermal dilatation (10⁻⁶ mm/mm × °C)	-26	-12	-11	3	2	2
Higryc dilatation (%)	0,649	0,199	0,417	0,033	0,086	0,086
Drying index (IA)	0,30	0,80	0,76	0,75	0,64	0,69
Chromatic change (ΔE)	—	6	11	—	4	7

Table 2 - Variation of the main petrophysical properties in NYT (untreated and treated) after ageing tests. Disag = disaggregated

	NYT			
		salt crystallization	freeze-thaw cycles	salt spray
Weight loss	Unt	disag	-2	-2
	AES	disag	-4	-4
	ES	disag	disag	-4
Compressive strength variation	Unt		disag	
	AES		-17	
	ES		disag	
P-wave variations	Unt		-54	-15
	AES		-1,6	-6
	ES		disag	12
Porosity variation	Unt		disag	+4
	AES		disag	+13
	ES		disag	+17

Table 3 - Variation of the main petrophysical properties in VS (untreated and treated) after ageing tests. Not mes = not measurable

		VS		
		salt crystallization	freeze-thaw cycles	salt spray
Weight loss	Unt	-73	-6	-1
	AES	-1	-1	-2
	ES	-1	-1	-2
Compressive strength variation	Unt		not mes	
	AES		0,5	
	ES		-7	
P-wave variations	Unt		not mes	
	AES		-27	
	ES		-26	
Porosity variation	Unt		+3	+2
	AES		+4	+13
	ES		+9	+30

Ageing tests resulted very aggressive for NYT treated with ES. This is was probably due to the decrease in pore space that made the pressure of crystallization more effective. Moreover, alteration mechanism such as salt crystallization and freeze-thaw resulted more aggressive in stones with a high percentage of mesopores ($r < 1 \mu\text{m}$; Rossi Manaresi, 1976).

Another aspect to be taken into account is the poor chemical resistance of the organic products that causes in time the deterioration of the polymer. The pre-treatment of NYT with Antihygro turned out to be effective to contrast the weathering induced by repeated freeze-thaw cycles.

The treatments were very effective for VS: in fact, the weight loss in untreated stone induced by salt crystallization test was reduced as consequence of consolidation. Finally, the effects of exposure to salt spray had no macroscopic effect in the two stones.

In general we can say that 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 as a result of ageing tests (Winkler, 1997; Goudie, 1999) and this is probably true for NYT, regardless of treatment method.

CONCLUSION

The collected data represent a contribution to the understanding of material behavior after conservative treatments in conditions close to those in which the material will be placed.

The experimental study allowed to evaluate how properties of two lithotypes were modified notwithstanding similar open porosity values and pore radii distribution.

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

A pre-treatment with antishwelling 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.

It should be remarked that NYT has been widely used in the Neapolitan architecture although this material is definitely prone to weathering. Moreover, unsatisfying results are often obtained by treatments with commercial consolidants. The semi-inorganic products conventionally used are not able to improve the resistance to degradation of zeolitized lithotypes.

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.

REFERENCES

- de' Gennaro, M. & Langella, A. (1996): Italian zeolitized rocks of technological interest. *Miner. Deposita*, **31**, 452-472.
- de' Gennaro, M., Cappelletti, P., Langella, A., Perrotta, A., Scarpati, C. (2000): Genesis of zeolites in the Neapolitan Yellow Tuff: geological, volcanological and mineralogical evidence. *Contrib. Mineral. Petrol.*, **139**, 17-35.
- Deino, A.L., Orsi, G., de Vita, S., Piochi, M. (2004): The age of the Neapolitan Yellow Tuff caldera-forming eruption (Campi Flegrei caldera - Italy) assessed by $^{40}\text{Ar}/^{39}\text{Ar}$ dating method. *J. Volcanol. Geotherm. Res.*, **133**, 157-170.
- Goudie, A.S. (1999): Experimental salty weathering of limestone in relation to rock properties. *Earth Surf. Process. Landforms*, **24**, 715-724.
- Mietto, P. (1988): Carsismo e speleologia nei Monti Berici. In: "I Colli Berici natura e civiltà", Signum Ed., Padova, 226-241.
- Orsi, G., Civetta, L., D'Antonio, M., Di Girolamo, P., Piochi, M. (1995): Step-filling and development of a three-layer magma chamber: the NYT case history. *J. Volcanol. Geotherm. Res.*, **67**, 291-312.
- Rossi Manaresi, R. (1976): Conservazione nel passato della pietra e nei tempi attuali. Durata dei trattamenti. Ed. Polistampa, Firenze, 15 p.
- Scarpati, C., Cole, P., Perrotta, A. (1993): The Neapolitan Yellow Tuff - A large volume multiphase eruption from Campi Flegrei, Southern Italy. *Bull. Volcanol.*, **55**, 343-356.
- Stück, H., Forgó, L.Z., Rüdlich, J., Siegesmund, S., Török, Á. (2008): The behaviour of consolidated volcanic tuffs: weathering mechanisms under simulated laboratory conditions. *Environ. Geol.*, **56**, 699-713.
- Winkler, E.M. (1997): Stone in the Architecture: Properties, Durability. 3rd Edition, Springer-Verlag, Berlin, 313 p.