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COMPACT LIMESTONES AS HISTORICAL BUILDING MATERIAL: PROPERTIES OF THE TRANI STONE (APULIA, SOUTHERN ITALY) AND PRELIMINARY STUDY FOR SELF CLEANING TREATMENTS

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Abstract

In this paper we deal with an experimental activity aimed to the characterization of a compact local limestone, named Trani stone. Compact limestones are very common materials used in the monumental and historic built heritage. In particular, with reference to the Apulian region (Southern Italy), they are the constituent stones of the numerous Romanesque Cathedrals, as well as of many other important monuments such as the UNESCO site of Castel del Monte. They have also been employed for the building of the fortified towns and norman-swabian castles facing the sea. The study reports mineralogical-petrographical and physical features, with particular reference to the behaviour with respect to the water. Ultrasonic tests have also been performed as indirect tool for the qualification of the stone in dry and wet conditions. A superficial treatment with photocatalytic titania (in water and alcoholic solution) has also been applied to the stone, in order to study the potential use of self-cleaning and anti-pollution nanotitania coatings for stone surface protection; a preliminary assessment of the morphology and distribution of the titania films on the stone surface and related colour changes has been carried out.

Keywords: compact limestone, physical characterisation, stone protection, nanotitania coatings

1. Introduction

Compact limestones are very common materials used in the monumental and historic built heritage, thanks to their large availability, workability and attractiveness. Many varieties of limestones can be found and they are selectively used as building or ornamental stones in minor buildings and monuments (Siegesmund and Török, 2011). Compact limestones mainly undergo to superficial decay, that includes dissolution of the soluble carbonatic components, sulphatation processes, deposition of substances coming from the surrounding environment (Bell, 1993). Dirt on the surface is a threat for the conservation of the stone surface, other than a drawback from an aesthetical point of view. This problem has been increasing in urban contexts, where the impact of the dirt makes the cleaning a relevant work within the conservation activities; moreover it also makes the maintenance for the preservation of the integrity of the surface very expensive due to the frequency that would be required. With reference to this problem, advantages could arise from the application of new advanced products, such as photocatalytic TiO_2.

Compact limestones are widely spread in the Apulian region (Southern Italy), due to the geological context of this area. The cultivation of these stone materials dates backs to the ancient times; until nowadays it has been a relevant economic resource for this area and the stone exploitation and trading is one of the most important activity in the region. Other than the common building materials in minor built heritage that give a typical fingerprint to many local historic towns, compact limestones are used in the numerous Romanesque Cathedrals of high artistic and architectural value, as well as in many other relevant monuments such as the UNESCO site of Castel del Monte. They have also been employed within the fortified towns and norman-swabian castles facing the sea.

Among the Apulian limestone, the "Trani Stone" is the object of the present study, aimed at characterizing the material for conservation purpose. The mineralogical-petrographic and physical features have been investigated. With reference to its conservation, the attention has been devoted to explore the possibilities of application of new advanced products, such as photocatalytic TiO_2. Two experimental nanotitania-based products (in water and alcoholic solution) have been applied to the stone, in order to study the potential use of self-cleaning and anti-pollution nanotitania coatings for stone surface protection. The basic assessment of the treatments has been carried out, by studying the morphology and distribution of the Titania films on the stone surface and the related colour changes.

2. Stone characterization

2.1 Mineralogical-petrographical and porosimetric features

Mineralogical-petrographic features have been investigated by *optical microscopy with transmitted light, using a* Zeiss microscope. Porosimetric analyses have been carried out by *mercury intrusion porosimetry* (Carlo Erba Porosimeter 4000); integral open porosity and pore size distribution have been determined, according to the NorMaL Recommendation 4/80 (Raccomandazione NORMAL 4/80, 1980).

Trani stone is a very well cemented grainstone (Dunham, 1962) (Figure 1). It has a grain supported texture, with the allochemical components mainly made of fossil's fragments (pelagic foraminifera, nummulites, ostracods and miliolidi) having fine to medium size (80-300µm); macrofragments have also been sometimes observed. The spatic calcite cement is present between the grains and in the inner fossil pocket, forming a crystalline mosaic that close almost the voids.

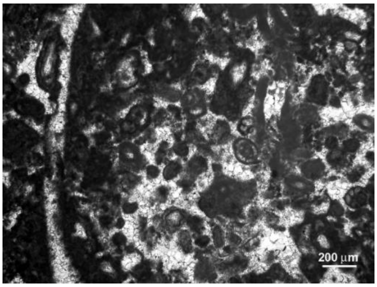


Figure 1. Trani stone photomicrograph (thin section, crossed nicols)

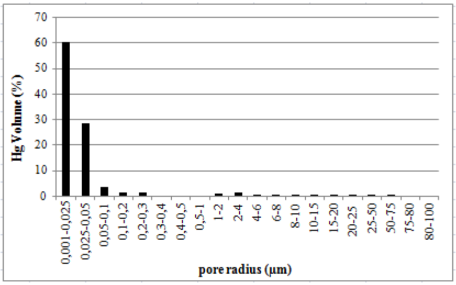


Figure 2. Pore size distribution

Trani stone is a very compact limestone. The integral open porosity measured by MIP is very low (4%); the pore size has unimodal distribution and is mainly made of smallest pores (between 0.05 and 0.001 microns) (Figure 2).

2.1 Physical properties

The following tests and analyses have been carried out:

- *measurements of the ultrasonic wave velocity (Vp and Vs)* in dry and wet conditions, *by* direct transmission method and 1-MHz probes (4Plus Epoch, Olympus equipment), on cubic specimens of 10 cm. For each sample three measurements were taken along X Y Z directions and the mean values of Vp and Vs have been considered. The anisotropy index has been calculated as $ARS= (Vpmax-Vpmin)/(Vpmax) \cdot 100$ (Ruedrich et al., 2007). Vp, Vs and ARS have been expressed as the mean values on a total of 10 samples;
- *colour measurements* (Raccomandazione NORMAL 43/93. 1993), using a Chroma Meter Minolta CR 300 colorimeter; colour parameters have been referred to the CIELab space and ten measurements have been carried out on each sample area of 5x5 cm; the results are expressed as the mean values on a total of 5 samples ;
- *static contact angle measurements* (Raccomandazione NORMAL 33/89, 1989), by a Lorenzen and Wettre apparatus (Costech instrument); thirty measurements for each sample area of 5x5cm were performed; the results are expressed as the mean values on a total of 5 samples;
- *capillarity rise test* (UNI 10859, 2000) on10 samples measuring 5x5x2 cm; duration of the test 8 days;
- *contact-sponge test* (Vandevoorde et al., 2009); for this test a disc-shaped sponge, having an area of 22.06 cm^2, has been soaked with 5 ml of water and pressed against the stone surface for 1 minute; water absorption has been calculated as $Wa= (m_i - m_f)/ (A \cdot t)$,where m_i is the initial weight of the sponge with water, m_f is the weight of the sponge after the application to the stone surface, A is the sponge area, t is the contact time; six measurements were performed and the reported data were expressed as the mean values;
- *total immersion test* (Raccomandazione NORMAL 7/81 1981) on 10 samples measuring 5x5x5 cm; duration of the test 12 days;
- *evaporation test* (Raccomandazione NorMaL 29/88, 1988) on 10 samples measuring 5x5x5 cm; duration of the test 9 days;
- *water vapour permeability test* (Raccomandazione NORMAL 21/85, 1985) on 10 samples measuring 5x5x1 cm.

The compactness and the high quality of the stone correspond to high ultrasonic waves propagation along X, Y and Z directions, in wet and dry conditions (Table 1). Similar values of the ultrasonic velocities have been found in both silicatic and carbonatic compact stones (Fort et al., 2011). The anisotropy index ARS give a very low value (2%), meaning a negligible anisotropy.

Table 1. P and S wave velocity in dry and wet conditions

Sample condition	**Wave**	**Wave velocity (m/s)**			**ARS (%)**
		X	**Y**	**Z**	
Dry	VP	6238 ± 199	6274 ± 188	6141 ± 122	2.12
	VS	3421 ± 26	3440 ± 269	3369 ± 88	
Wet	VP	6459 ± 216	6620 ± 243	6391 ± 82	3.46
	VS	3333 ± 124	3375 ± 114	3265 ± 55	

The values of the L *, a * and b *colour parameters of the stone are reported in Table 2. The low standard deviation values denote the homogeneous colour of the stone.

The very low stone porosity lead to a water-stone contact angle of 45°.

Table 2. Summary of the physical properties of Trani stone.

Integral open porosity [%]	3.7 ± 0.3
Prevailing range of pore radius [μm]	0.025-0.001
Colour parameters	L* = 87.07 ± 0.28 a* = 1.36 ± 0.05 b* = 8.84 ± 0.21
Water-stone contact angle [°]	46 ± 5*
Water absorbed by the “contact sponge test” (Wa) [$mg/cm^2 \cdot min$]	0.76 ± 0.04
Total water absorbed by capillarity (Q_{ft}) [mg/cm^2]	69.46 ± 2.69
Capillary absorption coefficient (CA) [$mg/cm^2 \cdot s^{1/2}$]	0.32 ± 0.02
Capillary absorption index (CI) [$mg/cm^2 \cdot s^{1/2}$]	0.83 ± 0.01
Imbibition capacity (IC) [%]	0.38 ± 0.09
Dying index (DI) [%]	0.13 ± 0.02
Water vapour permeability ($g/m^2 \cdot 24h$ at 20°C)	28 ± 4

The hydric behaviour of the stone is depicted in Figures 3, 4 and 5. The stone absorbs low amount of water by capillarity (70 mg/cm^2, corresponding to a weight increase of 1.35 ± 0.06%). The most absorption (90% of the total water amount) takes place throughout the first 24 hours. In the same way the water uptake by total immersion is very limited; the recorded imbibition capacity (IC) is 0.4% ca.

With reference to the drying, the most water loss by evaporation takes place during the first 24h (72%) and the residual water within the samples after 3 days is 10%; negligible water content has been recorded after 10 days.

The water vapour permeability of the stone is 28 g/m^2 per 24 hours.

All the parameters coming from the analyses and tests are summarized in table 2.

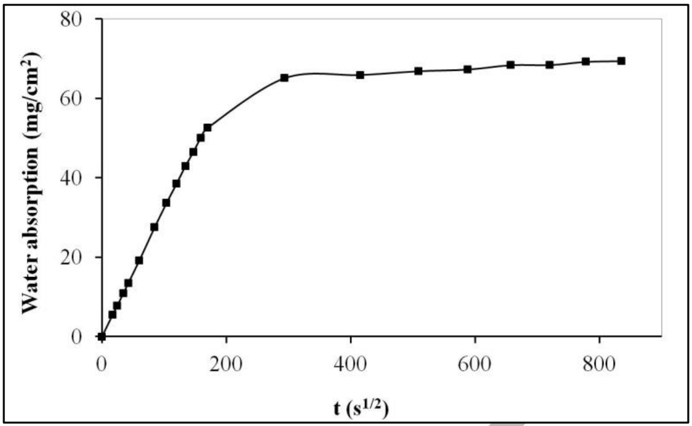


Figure 3. Capillarity water absorption curve.

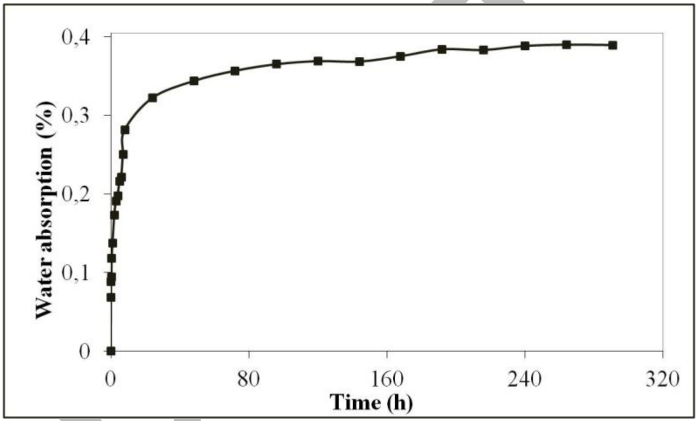


Figure 4. Total immersion water absorption curve.

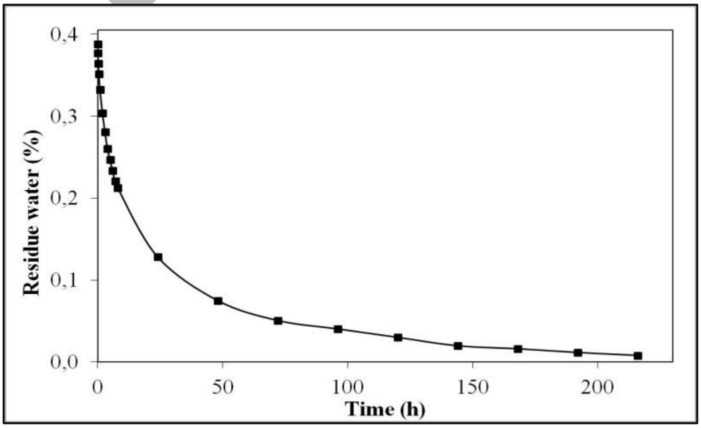


Figure 5. Water evaporation curve.

3. Application of the Titania coatings

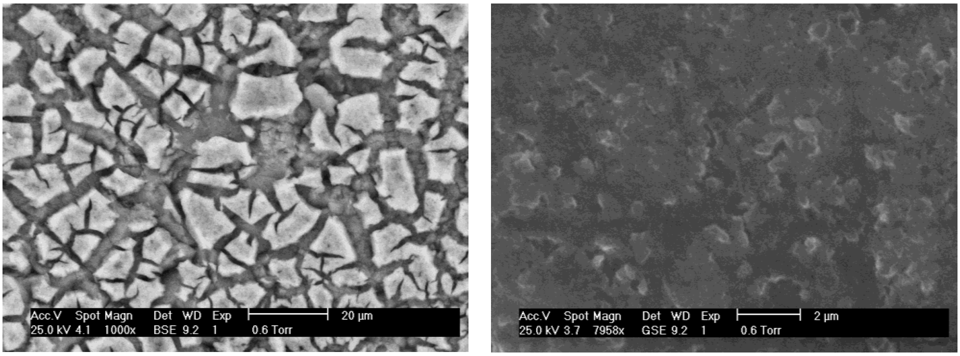
Titanium dioxide in the anatase form has proved to be an attractive compound, thanks to its chemical stability, non-toxicity and moderate price, to working as a preventive protection system activated by solar and UV light exposure. The efficiency of commercial and experimental titania coating as self-cleaning treatments on building stone materials has been recently investigated (Licciulli et al., 2011; Potenza el al., 2007; Luvidi et al., 2010; Quagliarini, 2012; Quagliarini, in press; La Russa, 2012). Two titania based experimental products has been selected for the application on the Trani stone.

Titania sols have been synthesized through the sol-gel technique starting from tetrapropylorthotitanate (TPOT) as titania precursor (Licciulli et al, 2011). Distilled water or a commercial solution of propanol, buthanol and ethanol have been used as solvents. The TiO_2 concentration within the solution is 1% by weight. The titania films have been applied on the stone specimens by spray coating, using a H.V.L.P. (High Volume – Low Pressure, AKOKA Model H2000A) spray gun (1 mm nozzle diameter, operating pressure: 2 bar).

The amount of the applied solution is 18.6 and 37.8 g/m^2 with reference to the alcoholic (TAL) and aqueous (TAQ) products, respectively. It has been determined by weight measurements, before and after the treatment of the stone specimens. After the application of the products, the samples were kept in laboratory environmental conditions (23 ± 2°C and 50 ± 5% relative humidity). Then the treated stone surfaces have been subjected to *morphological observations by scanning electron microscope (SEM)* in order to study the distribution and characteristics of the coatings on the stone surface. Investigations have been carried out on samples without metallisation, in “low vacuum” mode (0.6 torr, 25kV), using an Environmental-SEM (mod. XL30, FEI Company); both secondary (GSE) and backscattered (BSE) electron detectors have been used for the morphological observations.

Colour measurements have been also performed in order to assess if the films alter the original chromatic features of the stone surface.

The first problem related to the application of the titania coatings consists in the realization of a continuous and homogeneous film on the surface of the stone. The coating issued from the alcoholic sol (TAL treatment) appears to be characterized by extended micro-cracks (Figure 6a). On the contrary, good results have been obtained by the TAQ treatment. A continuous coating, uniformly distributed on the stone surface has been obtained by the application of the aqueous solution (Figure 6b), and any fractures have been observed in this case. The quick evaporation of the alcoholic sol and the rapid precipitation of the titania with the subsequent formation of cracks, account for these results. Micro-cracks on the coatings have been observed in a previous study (Licciulli et al, 2011) as depending on the solution’s concentration.



A b

Figure 6. ESEM images of the stone surfaces treated with a) TAL and b) TAQ.

The application of the titania films has been found do not alter in a significant way the original colour of the stone surface. Colour variations of 1.24 and 0.68, in terms of ΔE values, were measured on the stone treated with the aqueous and alcoholic solution, respectively.

4. Conclusions

The knowledge of the characteristics of the building materials used within the hystorical-architectural heritage is the basic condition for conservation purpose. Properties of the stones are the reference parameters for the choice of the conservation treatments and the evaluation of their performance. With this regard, other than the well-known technical characteristics related to the stone qualification for the trading at nowadays (Addabbo et al., 1985; Maggiore, 1983; Radina, 1956; Zezza, 1974; AA.VV. 1982), the work here carried out gives additional information on the stone properties of local historical building materials that is of interest in the conservation field. Among the building stones (Siegesmund and Dürrast, 2011), Trani stone is a material of high quality. Its high compactness, low porosity and behaviour to the water absorption account for the performance observed within the numerous buildings and monuments that have been realised using this stone. Differently than for the porous stones widely used in the same context of the Apulian region, whose relevant problem is the deep penetration of the agents of the decay and the consequent heavy loss of materials from the surface, Trani stone mainly undergo to the superficial decay. Dissolution processes and dirt deposition on the surface have been the main decay problems along the time, that have relatively compromised its conservation. Further threat in the last decades is coming from the pollution in urban environments, that is also responsible of the increase of the deposition rate of the dirt on the stone surfaces. With reference to this problem, it could be advisable to verify the possibility of the application of new advanced products, such as photocatalitic TiO_2 and the advantages that could arise from their use for stone treatments. Promising results have been obtained in order to the application of the water based experimental solution, in terms of morphological characteristics of the film and colour integrity of the stone. In addition the use of the water instead of the other chemical solvents has undoubtedly lower impact with respect to the environment and workers during the on-site application. These first basic aspects come from a preliminary activity within a work in progress, devoted to the evaluation of the possibilities and limits of new advanced products that, increasingly on, are proposed for stone conservation .

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