Workability and chemical-physical degradation of limestone frequently used in historical Mediterranean architecture

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***Abstract* – Sedimentary rocks are among the most used in historical buildings, as they are more readily available in the area and because they are also more easily extractable, in virtue in general of lower mechanical resistance. among these the most used are limestones and sandstones. The former are represented by a remarkable variety of lithologies, with highly variable characteristics, passing from the almost pure, massive and not very porous limestones, to those with a variable arenaceous-clayey component which instead are characterized by a low compactness and consequent high porosity (up to 35%).**

In this study the calcarenites present in two geographic sectors of Sardinia are dealt with, by comparing them with similar showers present in other territorial contexts of the Mediterranean. The mineralogical-petrographic analyzes by optical microscope and XRD analysis of the "Pietra Cantone" limestone of Cagliari (south Sardinia) show, besides calcite, the presence of phyllosilicates and various other accessory minerals. SEM analyses show a very weak physical-mechanical microstructure.

I. INTRODUCTION

Stone has always represented an essential georesource in human life, both for the production of weapons and tools for war use, and for the creation of everyday tools for hunting, rather than for cutting and processing other materials such as wood, etc.. In historical times all the most varied lithologies present on the earth's surface have been used, often also coming from places very far from the place where they will be worked, but the choice to use one rock rather than another is it has often been conveyed by the same intrinsic properties of stone materials. Undoubtedly, in the criteria for choosing the type of stone, leaving aside the socio-political reasons of some historical periods (e.g., Middle Ages) that have conditioned the supply of geomaterials on several occasions, the first factor is the possibility of an easy supply, possibly as much as close as possible, especially as regards the works that are important from the point of view of the quantities of materials processed and placed in the building.

Fig. 1. Figurative representation of the workers involved in a medieval construction site (from https://restaurars.altervista.org/wp-content/uploads/2015/11/fot.12.jpg)

But an essential and conditioning factor in the choice is represented by the workability of the stone. It often also involves the search for a geomaterial distant from the place of processing, especially when the local stone does not meet the technical needs of the craftsman or builder or artist. Workability is unconditionally the factor that cannot be ignored, as it conditions both the extraction techniques and the type of finishing process to be adopted. The study of physical-mechanical and technical characteristics of rocks represents an important preliminary phase in the careful and rational choice of the most suitable material for the realization of stone artefacts.

A. Use of stone and petrophysical properties

There are numerous properties and significant characteristics that must be considered for a correct use of the stone in the constructions; among these, certainly some physical characteristics (porosity, permeability, resistance to alteration), rather than the mechanical properties (hardness, resistance to compression or flexion), are indispensable for verifying the physical-technical suitability of a material for a specific use (or function) in the context of a work created by man.

For a correct interpretation of these physical and mechanical characteristics of the rocks, it is essential to have a good knowledge of the composition and of the structural and micro-textural characteristics of the materials. Moreover, a direct study on the rocky outcrop from which it is intended to extract the material would also be necessary, which can detect other important parameters in the opening of a quarry, such as the presence of joints or lithoclases, the alteration state, the presence of fissuring or fractures, of macroporosity, etc. All these properties and parameters can now be precisely determined today through physical-mechanical laboratory tests and even sophisticated instruments, perhaps accompanied by an accurate mineralogical and petrographic analysis, aimed at characterizing and classifying the lithotypes to be used.

Undoubtedly, in ancient times, except for recent periods, these physical characteristics and parameters could not be determined. However, the historical use of natural materials, such as stone, deriving very often from experience and intuition transferred over the centuries, has been handed down continuously in the historical period to the various builders and workers (Fig. 1). Even today, through the scientific research of some disciplines (applied petrography, mineralogy, chemistry), aimed at the knowledge of building materials of Cultural Heritage, we deepen our knowledge on production technologies (e.g. natural pozzolanic hydraulic mortars) and processing of geomaterials in antiquities. In fact, as we all know, from the careful examination of ancient buildings, clear indications can be drawn about some peculiar characteristics of the rocks and their vocations of use. Among the most easily workable rocks there are pyrolastitc and sedimentary rocks, very present in Sardinia, among which certainly those of carbonate origin (e.g., limestone, calcarenites). They show good propensity to be easily worked both in the extraction and in the finishing processing, even if in some circumstances (i.e., sandstones) it is not possible to reach too high levels of surface finish in terms of sanding and polishing.

B. Decay of carbonate sedimentary rocks

Carbonate sedimentary rocks (e.g., limestone, sandstone, etc.), especially those belong to Miocene, are widely used in the construction of historical buildings in Sardinia island as well as in many Italian monuments or other Mediterranean countries, from Punic–Roman to Romanesque times.

Generally, the more used stones belong to the sedimentary and volcanic stratigraphic sequence widely outcropping within the Sardinian Oligo-Miocenic rift [1-10]. In the Cagliari area (Southern Sardinia) the Pietra Cantone and Tramezzario calcarenites are the more used stones for construction of ancient buildings. The chemical–physical decay of these rocks is mainly due to the dissolution processes of carbonate cement. Due to the presence of clay phases in the matrix of stones, the decay is also due to the hygroscopic volume variations of these minerals and sea salts, which are present in the rock and that make the limestone easily degradable with a decrease in mechanical strength. When the limestone is used in the structural elements of monuments (e.g., ashlars of wall, column and jambs), the decay can lead to the formation of serious static-structural criticality in the buildings, as a strong retreat of vertical profile of the facade or detachment of the material portions from the decorative working parts, due to exfoliation and flaking processes.

To prevent such decay of carbonate sedimentary rocks which are used in the monuments, efforts are numerous in regard to their water protection and surface consolidation, from ancient time to laboratory experimentation. These chemical treatments differ both in typology of products and in application methods. However, due to the different chemical, physical and petrographic characteristics of these lithologies, microclimatic conditions and alteration degree of the artefacts, the conservative techniques must be adapted to each case individually.

C. Context of research and aims

There are numerous monumental examples in the territory of Sardinia in which the Quaternary carbonate rocks were extensively used already in Roman times, such as the port cities of Karales (today Cagliari) Nora, Bithia, Tharros, Turris Libisonis (today Porto Torres) [11], and numerous other less known archaeological areas, particularly vulnerable due to the action of the sea, the ungoverned runoff of meteoric waters. In such situations, wind erosion and the disintegrating action of the salts conveyed by aerosol or by capillarity in the materials intervene to make the material loss more incisive (crumbling and pulverization). Among these particular attention and suggest a preventive conservation intervention, are the western sector of the city of Turris Libisonis, arranged along the slope of a hill facing north, located along the coast line in the full urban fabric of Porto Torres, as well as the he area of Cabras, facing the sea to the east, on which the important archaeological area of Mont'e Prama [12-13] is located, which has returned a substantial number of sculptures, dated to the Nuraghic age, between the Late Bronze and Iron Age, 11th-8th century B.C.. In this case, rainwater is currently channeled into the narrow sector already excavated, enhancing its vulnerability and undermining its conservation. The natural and accelerated runoff of water transports and deposits the materials of surface erosion, continuously changing the state of the places.

The aim of the research is to analyse the geomaterials used on the monuments of Mont'e Prama Nuragic archaeological site (Fig. 2) and on the Roman Tharros village, taken as case studies, in which there are evident degradation processes of carbonate rocks, with the scope of understanding how the intrinsic properties of the material related to the environmental conditions affect the development methods and the nature of decay.

II. ANALYTICAL METHODS

Geological survey on the field and laboratory investigations on samples taken from the monument study-cases of archaeological sites, were carried out according to the following operative phases: i) stratigraphical study of rock outcrops; ii) macroscopic analysis of the archaeological materials; ii) in situ mapping of the macroscopic lithological characteristics of geomaterials, including the decay forms and conservation state; iii) sampling of materials, in agreement with the representativeness of the lithotypes (according to Recommendations Nor.Ma.L. 3/80, 1980); iv) optical mineral-petrographic, petrophysical studies; v) mineralogical studies by X-Ray Powder Diffraction (XRPD) analyses; vi) mineralogical and morphological studies by Scanning Electron Microscope (SEM) investigations.

The samples were collected from the shallow parts of the monument masonry, collecting volumes of about 20 cm^3, according to the recommendations of the local Superintendence of Cultural Heritage, which imposes strict limits on the quantity of sample to be collected. The volumes collected are however representative and adequate for the analytical studies.

Prismatic-like specimens were made up on laboratory for determining the physical properties; covered polished thin sections, about 30 μm thick, were also made up for both the optical microscopy and SEM studies.

Mineral assemblage of rock samples was determined using XRPD analytical technique on samples collected.

Fig. 2. Aerial view of Mont'e Prama archaeological site (Sinis, Central-West Sardinia).

Data were collected by a Rigaku Miniflex II apparatus, equipped by a monochromator, using Cukα radiation, at 30 kV and 30 mA, filter Ni, from 3-90 °2θ, and measuring step 0.02 °2θ. Mineral identification was carried out by JADE 5.0 software using the JCPDS (Joint Committee on Powder Diffraction) Data Base (2010) for search-match phase. The quantitative analyses of some representative samples were performed using the MAUD (Material Analysis Using Diffraction) analysis program mainly based on the Rietveld method.

SEM investigations and photomicrographs were performed on undisturbed rock specimens and on metallized polished thin sections with a Zeiss Evo LS 15, equipped with a LaB6 filament as electron source, for providing information about textural parameters of representative samples (fibrous, lamellar, compact, porous morphologies). Energy Dispersive Spectrometry (EDS), by using the INCA OXFORD apparatus equipped with LaB6 as electron source and a solid-state detector X-Max 50 mm, allowed verifying the qualitative presence of chemical elements of specific interest.

Porosimetry of rock samples has been performed by a Hg-porosimeter AutoPore IV 9500 Micromeritics.

The absorption test by capillarity was performed according to the UNI 10859 standard.

III. RESULTS

A. Mineralogical and petrographic features

Below are the compositional characteristics of the sandstones used in the monuments located in the coastal area and characterizing the Nuragic archaeological site of Mont'e Prama and the Roman village of Tharros (central-western Sardinia).

Fig. 3. Sandstone under reflected light microscopy

These geomaterials show high susceptibility to meteoric water through chemical-physical decay processes (i.e., dissolution of carbonate cement, disintegration by decohesion and consequent loss of material, Figs. 3, 4), strongly guided by the microstructural characteristics and the local marine microclimate [14]. The significant XRD patterns resulting from the semi-quantitative interpretation (Rietveld method) show a high heterogeneity. Bioclastic sandstones have the following mineralogical composition: calcite (70.3 ± 12.0%), quartz (6.4 ± 4.4%), plagioclase (8.4 ± 5.3%), K-feldspar (1.7 ± 0.4%), biotite (0.6 ± 0.3%), muscovite (about 0.7%). The compositional variability of these lithologies, evident both at the scale of the outcrop and that of the artifacts, is due to the irregular sedimentological compositional nature and the consequent irregular diagenesis from which these materials originate. In fact, these are muddy offshore deposits (continental shelf) of the Miocene age, and coarse coastal deposits formed by gravels and carbonate cement sands, even with cross-stratification, rich or very rich in fossil associations referring to the Quaternary (Tirreniano Autc.) [15, 16]. These rocks are therefore affected by local contributions, bathymetric variation, sediment reprocessing and the ways in which the modeling agents have eroded, selected, deposited and cemented the clastic components.

Under polarised microscopy, these rocks show the textural characteristics typical of a carbonate cement grainstone, with sub-rounded, abraded clasts, with variable sorting, very rich in bioclastic components, which are predominant. In the conglomerates and coastal terrigenous sandstones, there are quartz, plagiolase and K-feldspar.

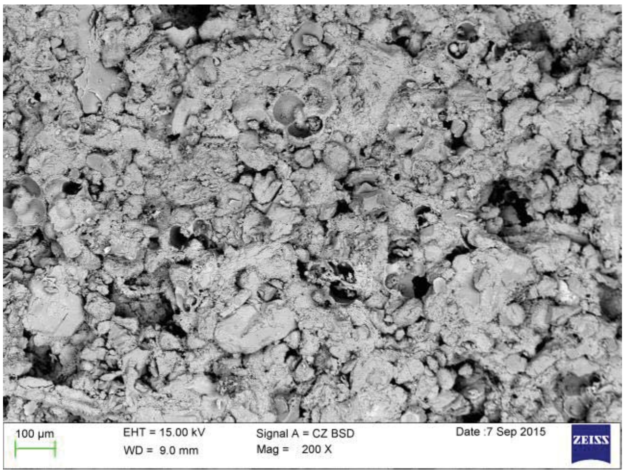

Fig. 4. Sandstone under SEM microscopy

B. Physical properties of sandstones

Table 1 shows the values of some physical properties (porosity, water absorption by capillarity) critically important for the susceptibility to water and for the durability of sandstones. Their behaviour, albeit with considerable differences in grain and texture, is critically controlled by the cementation degree of the stone components and by the nature and size of the bioclasts; the framework of these elements strongly affects the porosity and the water absorption capacity. About 90% of the water is absorbed in 40 minutes for coarse-grained sandstones and in 25 minutes for medium-grained ones (Figs. 5, 6). The kinetics of desorption by evaporation are quite rapid: about 90 hours for coarse-grained sandstones and 60 hours for fine-grained ones.

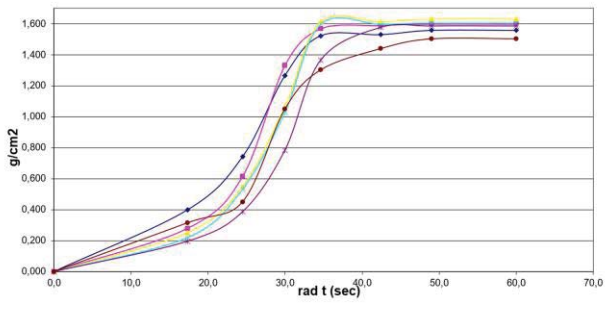

Fig. 5. Kinetic of water absorption by capillarity (according to UNI 10859) of coarse sandstone samples

The distribution of pores is characterized by large voids, concentrated in the 100-10 µm range, with deviation of the average radius towards smaller dimensions for finer-structured sandstones.

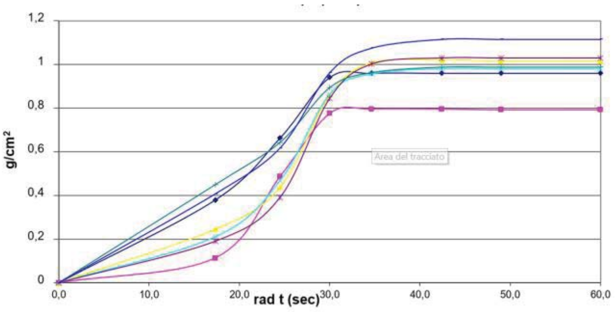

Fig. 6. Kinetic of water absorption by capillarity (according to UNI 10859) of medium-coarse sandstone samples

Ultrasonic speeds are conditioned by density and cementation; the sandstones have low values of ultrasonic speeds and mechanical resistance. The saturation condition causes a significant loss of performance. The dimensional stability measurements to water on long prismatic specimens, showed a slight tendency to expansion, in the saturation phase and shrinkage in the desorption phase. It is about ten µm / m, which, although they may seem irrelevant, are the cause of a bad elastomechanical agreement, as well as the onset of micro-fractures during the curing of TEOS-based consolidating devices (PM) [17].
The lithologies briefly described are intrinsically susceptible to the interaction of water, subject to rapid material loss due to receding and wear of the surfaces, thinning of the wall thicknesses until collapse. The consolidation and protection processes, considering the microstructural aspect of these materials, are very complex and require continuous experimentation to find new aids [18, 19] capable of generally more resistant and stable intergranular sutures.

IV. DISCUSSION AND CONCLUSIONS

The example described with the case studies of monumental complexes, archaeological areas, materials of the structures, intends to set a reference for the continuous verification of the analysis of the causes of the monument-water interaction and of the possible solutions to be considered for the different stairs.

The state of conservation of the monuments, also in relation to the activities of use and enhancement, activates a dynamic that must be continuously monitored. The main vulnus is given by the state of ruin, which opens the way to multiple degradation factors, including water, which runs through the surfaces of the individual units, penetrating the unprotected body of the structure. Relating these factors to the more than 8,000 nuraghes and about the thousand available for use indicates the size of the problem.

Table 1. Average values (6 samples) of some physical properties of sandstones: bulk density (ρ_b); porosity Mip (ΦMIP); coefficient of capillarity absorption (A.C.) e asintotic coefficient (M); imbibition coefficient (C.I.$_W$); ultrasonic velocity (Vus); anisotrpic index (I.A.$_{US}$) maximum (DMax) and minimum (DMinof ultrasonic velocity; dry and wet compression strength (σ_c).*

ρ_b (g/cm^3)	**Φ_{MIP}** (%)	**A.C.** (g/cm^2)·t^{½}	**M*** (g/cm^2)
Sandstone with carbonate cement, mediun coarse (Tharros samples)			
1,87±0,52	20,1±2,5	0,017±1,130	0,96±0,09
Sandstone with carbonate cement, coarse (Tharros samples)			
1,59±0,36	31,5±2,7	0,025±1,482	1,58±0,05
Sandstone with carbonate cement (Mont'e Prama Tombs samples)			
1,69±0,72	28,6±4,9	0,027±1,531	1,68±0,06

C. I.w (%)	**V$_{US}$** (m/s)	**I.A.$_{US}$** (%)	**σ_c (MPa)**
Sandstone with carbonate cement, mediun coarse (Tharros samples)			
		DMax	σcDry
		1,89±1,06	14,3±1,2
11,80±0,53	3284±145	Dmin	σcWet
		1,74±0,85	11,5±1,3
Sandstone with carbonate cement, coarse (Tharros samples)			
		DMax %	σcDry
21,14±1,94	2674±121	1,89±1,06	5,24±1,5
		Dmin%	σcWet
		1,74±0,85	4,12±1,4
Sandstone with carbonate cement (Mont'e Prama Tombs samples)			
		DMax %	σcDry
21,7±2,12	23241±92	2,03±1,58	4,35±1,4
		Dmin%	σcWet
		1,63±0,61	3,54±1,2

Even the conservation of coastal archaeological sites, characterized by highly valuable materials, in aggressive environmental exposure classes, highlights still unresolved criticalities and difficulties deriving from the need to remove harmful substances from porous matrices and from the incessant search for consolidants and protective agents capable of carry out their action effectively, however not sufficient if not accompanied by other conservation actions referred to the general environmental context. The deterioration process is enhanced by the almost absence of ordinary maintenance, which is essential for the defense of the status quo ante. In some cases, if the archaeological emergencies are limited by extension and high, the specific coverages can slow down the effect of rainwater, but when the areas are extensive and the elevations are considerable, the protections that can be hypothesized not only cannot be realized, but not even configurable in safety and in operation. Each single monument can contain within itself and suggest possible solutions, only if it is interrogated with all the tools available. Often the lack of documentation on the work carried out and on previous laboratory investigations, abandonment and neglect limit data collection. The design interventions to stem the negative effects of water on monuments cannot ignore the reference landscape and the specific context; in the case of nuragic monuments dedicated to the cult of water, the primary objective is above all to respect the balance achieved by the structures over the centuries and millennia, to govern the innate and consolidated interaction. In the case of coastal sites, also the restoration of natural drainages and the reconstitution of spontaneous vegetation, as a natural element of dampening wind erosion and partial interception of runoff waters and the saline contribution to the structures, would certainly need to be evaluated and strengthened with a view to integrated and preventive conservation.

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