DECAY PROCESSES IN SEDIMENTARY STONES: A PETROPHYSICAL APPROACH

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INTRODUCTION

Several factors influence rocks durability in heritage field: processing technique, use, placing, environmental conditions, and, above all, petrophysical properties. The present work concerns the petrophysic analysis of lithotypes largely used in the Italian cultural heritage. For each specific use of stones, a crucial point in the characterization is to establish their durability (Inkpen et al., 2004). Durability, in built heritage field, can be defined as the property of a natural lithotype to last, in a specific environment and typology of use, maintaining its characteristics of strength and resistance to decay (Benavente et al., 2004). Inkpen et al. (2004) tried to address the factors influencing stone durability, with different results. Turkington (1996) linked durability with the rate and nature of the weathering processes affecting a rock, creating secondary alteration products. The most recent approach implies the prediction of rock behaviour through laboratory tests followed by analysis of several parameters and their relative variability (Turkington, 1996). Considering two of the main factor influencing durability (i.e., pore structure and water saturation), Richardson (1991) defined the connected porosity (Ø).

Further corrections to this model can be brought by introducing the durability estimators, that take into account different petrophysical parameters (e.g., pore structure, mineralogical composition, and strength) derived from the characterization of the stone (Benavente et al., 2004, 2007; Benavente, 2011).

These considerations point out that the two main characteristics to be addressed in order to predict decay are the void space (pore radius, distribution, shape, and connectivity) and the mineralogical-chemical composition of the material.

Work aim

Considering the conservation problems connected with the porous structure parameters, this thesis addressed the reciprocal influence of porosity and decay processes in four sedimentary lithotypes. The study aimed at characterizing the porous network of fresh and altered samples to highlight its evolution after decay processes. Such characterization assessed correlations between petrologic and mineralogical features and weathering processes.

Moreover, the combined use of several analytical techniques allowed evaluating the widest porosimetric range possible, estimating the relative resolution of each method. Also the influence on petrophysical properties of induced 3D pore network modification, such as water absorbance (both by total immersion and capillary uptake means), was investigated.

EXPERIMENTALS

Materials

The materials were chosen within the ornamental stones listed in the attachment A (A.2.11-Italy) of the technical EN 12440:2000 (Natural Stone - Denomination Criteria Normative). The selection criteria of the sedimentary lithotypes were: differences in minero-chemical composition and differentiation in the open porosity values. Particularly the study was addressed to the following lithotypes:

- Macigno Sandstone, a turbiditic sandstone, mainly composed by quartz and feldspars, secondary calcite and phyllosilicates, presenting bluish-grey fresh cut surfaces, with yellowish surfaces when altered;
- Breccia Aurora, a polygenic breccia consisting of nodules of compact limestone and micritic cement joints alternate with clastic texture;
- Rosso Verona, a biomicrite where the compact nodules of massive micritic matrix with microfossils is cut by veins of micrite and clay minerals;
- Vicenza Stone, a biologiclastic limestone often recrystallized and cemented by micrite carbonate matrix, rich in micro and macro foraminifera, algae, bryozoans and remains of echinoderms, with trace of iron oxides. The analysed types of Vicenza Stone differ for sorting of fossils and detrital sediments fining upwards within the same quarry.

The materials were characterized by means of mineralogical and petrographic analysis (Polarized Light Optical Microscopy - PLOM, Environmental Scanning Electron Microscopy - E-SEM, and X-ray Powder Diffraction - XRPD) in order to have a full knowledge of the textural and compositional parameters (Table 1).

<table>
<thead>
<tr>
<th>Lithotype</th>
<th>Classification</th>
<th>Texture</th>
<th>Grain size</th>
<th>Minerals [volume %]</th>
<th>Allochems</th>
<th>Porosity type</th>
<th>Open porosity [volume %]</th>
<th>Volume weight [g/cm³]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Macigno Sandstone  MS</td>
<td>turbiditic sandstone - greywacke</td>
<td>clast supported arenite</td>
<td>Qtz (55%) Ab (5%) Kfs (5%) lithoclasts (20%) phyllosilicates (10%) Cal (5%)</td>
<td>Inter-granular and intra-granular (inside phyllosilicates and altered minerals)</td>
<td>1.9±0.1</td>
<td>2.56±0.1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Breccia Aurora BA</td>
<td>brecciated limestone - intrapelite</td>
<td>brecciated structure</td>
<td>Cal (99%) Qtz (0.5%) Mnt-Cl (0.5%)</td>
<td>inter-granular</td>
<td>0.5±0.1</td>
<td>2.69±0.1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Rosso Verona RV</td>
<td>biomicrite nodular structure</td>
<td>Cal (98.5%) Qtz (0.5%) Ill (1%) oxides (traces) bivalve ammonites</td>
<td>inter-granular and intra-granular (inside phyllosilicates and altered minerals)</td>
<td>1.5±0.1</td>
<td>2.82±0.1</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Vicenza Stone VS</td>
<td>biomicrite clast supported calcarenite</td>
<td>Cal (99.9%) oxides and hydroxides (traces) nummulites foraminifer red algae sponges corals bryozoans</td>
<td>intra-particle inter-particle vug fenestral inter-granular</td>
<td>22.9±0.1 23±0.1</td>
<td>2.66±0.12</td>
<td>0.49±0.1</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Methods

Several analytical methods (direct or indirect) were developed to quantify porosity. The results of some measurements (e.g., Mercury Intrusion Porosimetry - MIP, X-ray Computed Tomography - XRCT, ultrasound speed) allowed us to infer the porosimetric distribution and the network and pore spaces characteristics (i.e., typology, shape, tortuosity, and connectivity). Other methods (e.g., total immersion, capillary rise, evaporation rate) allowed to parameterize only the features linked to porosity (i.e., anisotropies, water dynamics).

In this work both direct (i.e., density and total volume determination, Image Analyses - IA, XRCT) and indirect (i.e., MIP, hygroscopicity, total immersion, evaporation rate, ultrasound velocities, and capillary absorption) techniques were applied. Each porosimetric test has its specific measurement range, influenced by the resolution limits of each technique (Fig. 1).

Moreover mathematical modelling were applied to obtain pore related properties (e.g., hydraulic water front height, tortuosity) and a water porosimetry.

Artificial ageing

Durability of building materials is a key factor in cultural heritage conservation, especially considering the rising aggressiveness of the environment. A tool to test the durability of stones to the most diffuse
weathering mechanisms developing inside the porous network is represented by artificial ageing procedures. Such tests are laboratory simulation of accelerated natural processes.

In a relatively short time, accelerated ageing tests, although destructive, enable researchers estimating the alteration suffered by the materials when exposed to decay agents (Steiger, 2005; Espinosa et al., 2008; Buj & Gisbert, 2010).

The results give a picture of how the different factors (e.g., ice, salts, and air pollution) affect the materials under real conditions (Grossi et al., 1997; Laycock, 2002). Even if the relationship between test procedures and the natural weathering is approximated, the ageing tests are still employed for the relatively simple procedures, describing the reaction of porous stones to weathering mechanisms.

In this thesis only the two main deteriorating mechanisms affecting porous geomaterials were analysed by accelerated ageing test mechanisms. The tests are the salt crystallization (partial continuous immersion test; Benavente et al., 2001) and the pure water freeze - thaw cycles (following the UNI 11186:2008 protocol).

RESULTS AND DISCUSSION

Petrophysical characterization of the different lithotypes: before and after weathering

1) Macigno Sandstone

The fresh samples evidenced a mono-modal distribution of pore radius, whereas the altered samples showed a poly-disperse porosity, with a total increment of porosity and the appearance of 100 µm radius pores (Fig. 2a). The analysis of the porosimetric curves trends associated with the image and petrographic analyses, suggested that mechanical decay processes were active, generating cracks.

The micro cracks (radius < 0.1 µm) were probably due to the rupture of phyllosilicates along the layering, whereas the major cracks were linked with the rupture along grain boundaries, and along primary porosity.

The different techniques, within their resolution range, highlighted an increase in open porosity after weathering. The variance between hygroscopicity and MIP measurements of the micro-porous network parameters was addressed to the phyllosilicates in the matrix.

2) Breccia Aurora

The porosimetric reconstruction by petrographic analysis and petrophysical properties (i.e., ultrasounds, absorption rates) did not evidenced any decay process; therefore, the variability of the two porosimetric
distribution curves, referred to two different samples, was likely to ascribe to the natural variability of the rock (Fig. 2b).

![Graphs showing porosimetric trends for different samples]

Fig. 2 - Reconstructions of the whole porosimetric range (left), and comparisons between MIP and hygroscopicity (center unaltered samples, right altered samples). a) Macigno Sandstone; b) Breccia Aurora; c) Rosso Verona; d) Fine grained Vicenza Stone; e) Coarse grained Vicenza Stone.

3) Rosso Verona

It can be noticed that the fresh sample presented a mono-modal distribution, whereas the altered sample presented asymmetrical mono-dispersion porosity, with an overall increment of porosity (Fig. 2c).

The analysis of the porosimetric trends associated with the image and petrographic analysis suggested a mechanical decay processes, generating cracks, mainly along phyllosilicates layering and grain boundaries. All the different techniques registered an increase in open porosity, within their resolution ranges.

4) Fine grained Vicenza stone

The fresh sample presented a poly-disperse distribution (Fig. 2d) whereas the altered sample presented a total increment of porosity, with the shifting of the main peaks.

The analysis of the trends together with the image and petrographic analysis suggested that mechanical and chemical decay processes were involved, generating cracks, and a combination of dissolution (widening of pores at 0.2 and 100 µm) and re-precipitation (pore shrinkage at 9 µm). The different techniques registered an increase in open porosity, within their resolution ranges.

5) Coarse grained Vicenza stone

The fresh sample presented a bimodal distribution (Fig. 2e) whereas the altered sample presented a total increment of porosity, with the shifting of the main peaks.

The analysis of the trends obtained by image and petrographic analysis suggested that both mechanical and chemical decay processes were involved, generating cracks (micro cracks at 0.1 µm), and a combination of dissolution (widening of pores at 0.2 µm) and re-precipitation (pore shrinkage at 9-100 µm). The different techniques registered an increase in open porosity, within their resolution ranges.
Brief review of the methods

The association of different techniques was effective to evaluate the typology and porosimetric distribution of the pore network. The mineralogical and petrographic constrains obtained by SEM and XRCT, before and after weathering, coupled with XRPD analyses helped to define the constituents and the location of the voids inside the rock structure, as well as to recognize the minerals mainly connected with the weathering processes.

The image-based techniques allowed to sketch the pore shape and connection, evidencing the structural differences between the different lithotypes, and the modification induced by weathering. Particularly the IA based on SEM photograms defined a porosimetric range from 0.5 to 100 µm, with particular attention to pore volume and shape. Otherwise, XRCT helped to determine the three-dimensional porous range (about from 21 to 500 µm) giving a precise description of pore volume, shape, and connectivity, as well as a morphological three-dimensional reconstruction of the porous network.

The ultrasound measurements verified the evolution of anisotropy along S0 and/or bedding. The MIP analyses was useful in the reconstruction of the widest pore diameters range, and, in comparison with image-based techniques, allowed to infer pore typology and shape. Hygroscopic porosimetry was proved to be useful if coupled with MIP in presence of phylllosilicates and other hygroscopic minerals (or compounds), highlighting the possibility of RH variation to trigger the weathering due to swelling (Ruedrich et al. 2011; Gisbert & Galarreta Corcuera, in press). The mathematical model resulting for water porosimetry showed high potential for rocks with hardly connected porous network (BA, fresh MS, and RV), ad had a poor correlation for highly connected porosity (PV, altered MS, and RV). Further corrections, aimed at a thorough description of the three-dimensional characteristics of the porous network (connectivity, tortuosity, shape), might be developed exploiting permeability measurements (Fagerlunld, 1972). The capillary uptake and total immersion test results were strictly connected to the porous network and its modifications (e.g., crack openings, widening of holes, dissolution, and re-precipitation process).

CONCLUDING REMARKS

Specific findings related to the studied materials
- The Macigno Sandstone showed a great susceptibility to salt decay, with the formation of cracks along grain boundaries and in the interlayering of phylllosilicate minerals. After weathering the open porosity increased from 2% to 6-9%. Moreover, the presence of swelling minerals suggested the liability to hygrothermal stress.
- The massive structure of Breccia Aurora resulted resistant to the artificial ageing processes applied in this work. The brecciated structure implied natural variations in the sample set.
- Rosso Verona suffered both salt crystallization and freeze-thaw weathering, with formation of microcracks along interlayering of phylllosilicate (mechanical damage) and coupled dissolution-precipitation processes (chemical damage) at the expense of micrite. Salt crystallization generated the increase of open porosity from 1.8% up to about 9%. The presence of swelling minerals suggested also the predisposition to hygrothermal stress.
- The fine-grained variety of the Vicenza stone showed a high weathering rate. In particular: i) microcracks formed after ageing with freeze-thaw, and ii) mechanical and chemical stress developed after treatment with saline solution with a sharp increase of about 14% in open porosity (from 27% up to 41%).
- The coarse-grained Vicenza stone showed mechanical stress after freeze-thaw weathering and more pervasive chemical degradation due to salt weathering. Salt crystallization produced an increment in open porosity from 36% up to 44%.

Methodological concluding remarks
- The association of multiple techniques was needed to define the porous network of different stones and its evolution due to decay processes. In fact, the chance to combine several techniques allowed reconstructing a
wider porosimetric range, acquiring therefore the evolution of weathering between 0.002 to 250 µm. Moreover
the coupling of MIP and hygroscopic micro-porosimetry highlighted the presence of phyllosilicate and their role
in decay processes, contributing to the interpretation of the structural evolution of Macigno Sandstone.

- The mineralogical-petrographic support to the porosimetric datasets was fundamental to foresee and
interpret weathering modifications and involved processes (mechanical or chemical). For example, the presence
of oriented phyllosilicates in Macigno Sandstone and Rosso Verona, affected the structure since they were the
preferential site for the formation of crack openings (both for hygrothermal and crystallization stress). Moreover,
the presence of micrite (characterised by a high specific surface) in Vicenza stone and Rosso Verona suggested
the liability to chemical attack.

- The analysis of petrophysical properties (i.e., total immersion, capillary uptake, and ultrasounds) allowed
evaluating anisotropy formation and showed a direct correlation with the variation of porosimetric
distributions. Ultrasounds gave a direct estimation of the anisotropy coefficient of each lithotype and helped to
define the preferential orientation of crack openings in Macigno Sandstone, Rosso Verona, and Vicenza stone.
The absorption dynamics confirmed that the rocks liable to freeze-thaw ageing developed micro-cracks, showing
an higher absorption coefficient and that the salt crystallization processes lead to different textural modification,
both mechanical and chemical, the latter especially relevant in Vicenza stone where it caused a decrease of the
absorption coefficient.

- The model of porosimetric distribution based on capillary uptake measurement was consistent with the
other datasets for hardly connected porous network and have a poor correlation for highly connected porosity.
Further corrections aimed at a thorough description of the three-dimensional characteristics of the porous
network (connectivity, tortuosity, shape) might be developed exploiting permeability measurements (Fagerlund,
1972).

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