

# POROSIMETRIC CHANGES AND CONSEQUENCES FOR DAMAGE PHENOMENA INDUCED BY ORGANIC AND INORGANIC CONSOLIDATION TREATMENTS ON HIGHLY POROUS LIMESTONE

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## Abstract

Surface consolidation treatments on stone materials induce relevant modifications in the porous substrates that can potentially trigger deterioration phenomena not active in the same untreated materials. Unlike most protective products that form films on stone surfaces, consolidants must penetrate the first layers of the substrate in order to function, partially filling the voids of the porous network. Meso- and macro-porosities of Globigerina Limestone (Malta's highly porous sedimentary stone), before and after treatments with several organic and inorganic consolidants were investigated by means of N<sub>2</sub>-BET (Brunauer–Emmett–Teller) analysis. BET total inner superficial area together with pore size distribution data gave interesting information on preferential distribution of different products inside the open porosity network. The treatment can produce in some cases small changes in total superficial area (inorganic treatment), in some others cases a dramatic reduction (organic) and also an unexpected relevant increase (ethylsilicate). Pore size distribution shows shifts towards lower pore diameters turning a predominantly macro-porous system into a meso-porous one. These porosimetric changes have a direct relationship with the physical properties of porous building materials. In relation to the environmental context and the direct exposure to deterioration agents, the consolidation treatment can also have a negative impact for the conservation of works of art.

**Keywords:** BET, calcareous stone, consolidation treatment, porous materials, Malta Globigerina limestone

## 1. Introduction

Deterioration mechanisms on natural porous stones were widely investigated during the last decades, the main decay processes usually sought in chemical weathering, mechanical

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degradation and biodeterioration caused by extrinsic agents like air pollutants, soluble salts, fungal growth (Winkler, 2013). In order to slow down deterioration, to restore the original physical, chemical and mechanical properties of damaged materials and to combat the action of aggressive agents several methods of conservation interventions were developed. A part of them makes use of chemical products that, applied to buildings surfaces, act as a barrier to external deterioration causes with the aim of strengthening the intrinsic defences of historical works of art. From a general point of view it is possible to assert that the application of protective and consolidating products has an impact mainly on *surface* physical properties as colour, hydrophobicity, cohesion but the highly porous materials are deeply affected not only on their “external interface” but also on their “*internal interface*”, in other words in their porosity structure. And also if the protective products should exert their action only on the external surfaces, while consolidant must enter inside the materials by definition, literature data supports, without any doubt, evidence of substantial penetration of conservation materials inside highly porous substrates (Doehne E. and Clifford C.A., 2010). Despite the limited thickness of the impregnated layer compared to the bulk, a very small quantity of product can induce dramatic changes in physical properties of the entire artefact, like water uptake and vapour water permeability, and consequently in its durability (Ferreira Pinto A.P. and Delgado Rodrigues J., 2008).

Several studies and investigations have focussed on the evaluation of macroscopic physical property changes as a result of stone conservation treatments (colour, water absorbance and water vapour permeability, hardness etc.). These laboratory tests on stone samples or on experimental in situ-tests on building materials were often performed according to international standard methods (EN, ISO, UNI, UNI-NORMAL, ASTM, RILEM) with different non-invasive or quite simple procedures. Changes in macroscopic properties are strongly linked to changes in the microscopic structure of materials, nevertheless very few authors elaborate on changes induced by treatments in the microscopic properties of substrates by direct investigation of porosity. In fact, the analysis of porosity by optical methods (areal porosity determined on polished sections of samples), by mercury injection or gas expansion methods are invasive techniques and require a minimum quantity of material often of the order of some grams, not always easily sampled on artefacts.

The aim of the present research was the investigation of changes induced by organic and inorganic consolidant products after their application on a highly porous natural stone, the Globigerina Limestone, widely used as building material in the Maltese Islands. Modifications in the porosity network was investigated and some considerations on the correlations between these data and water sorption properties were discussed, being aware that a difficult goal is the interpretation and prediction of macroscopic properties of porous media with the help of microscopic pore structure models.

## **2. Materials and methods**

### **2.1. Globigerina limestone**

Samples of stone of *Globigerina Limestone* (Glob1, acquired as *Franka* type according macroscopic evaluation but discovered to be, after specific chemical characterization, a *Soll* type (Cassar J., Vella A. 2010)) were cut from a local quarry in Malta (n°44, near Mqabba) and previously characterised by SEM/EDS (cross-sections analysis with a LEO 1430, Oxford Link spectrometer with an ATW2 window for the detection of light elements) and calcimetric analysis (Dietrich-Frühling method) (Croveri *et al.* 2004). Glob1 is characterised by a CaCO<sub>3</sub>

content of 91% ( $\sigma = 0.5$ ). EDS microanalysis results are shown in Tab. 1 (5 areas, mean values expressed as percentage of oxides, standard deviation in brackets)

Tab. 1: EDS microanalysis of Glob1 substrates.

	CaO	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	MgO	FeO
Glob 1	91.0 (1.5)	4.8 (0.6)	1.9 (0.3)	0.9 (0.1)	1.7 (0.4)

## 2.2. Consolidant products and treatment methodologies

Samples (5×5×2 cm, 5×5×1 cm) were first conditioned following the UNI 10921 standard and then treated on one surface only. Inorganic treatments were carried out with aqueous saturated solutions of Ba(OH)<sub>2</sub>·8H<sub>2</sub>O and (COONH<sub>4</sub>)<sub>2</sub>·H<sub>2</sub>O (AmOx) in cellulose poultice (Arbocel BC1000) with a contact time of 5 and 6 hours, respectively. A 2-propanol dispersion [0.06 M] of nanosized calcium hydroxide particles (Salvadori B. and Dei L., 2001) was applied by brush (350 ml/m<sup>2</sup>). An ethyl silicate (Estel 1000, CTS, 500g/m<sup>2</sup>, SiEt), an acryl-silicon based polymer (Acrisil 201/O.N. 0,5 l/m<sup>2</sup>, CTS, Acrisil), a fluoelastomer (Akeogard CO, 50g/m<sup>2</sup>, Syremont S.p.A., AkCO), a perfluoropolyurethanic pre-polymer (Akeogard Z1074 –Edilgard<sup>®</sup> Wall, 50g/m<sup>2</sup>, Syremont S.p.A., Ak74) and a functionalised fluorinated polyurethane (Akeogard PU, 50g/m<sup>2</sup>, Syremont S.p.A., AkPU) were applied by brush.

## 2.3. Porosimetric analysis

Analyses of superficial areas and pore-size distributions were carried out with a surface analyzer Coulter SA3100 according to the BET model and BJH calculation using N<sub>2</sub> gas. The material analyzed was sampled from the treated surface taking the first 0,5 cm thickness. About 3-5 g of stone material was used for each analysis, replicated twice for each treatment. In order to compare the results of pore size distribution, the experimental data were normalized using the following equation:

$$V\%_N = V\% * (BJH_{tot\ TR} * W_{TR}) / (BJH_{tot\ NT} * W_{NT}) \quad (Eq. 1)$$

where  $BJH_{tot}$ : Total volume of pores (mm<sup>3</sup>/g)

$W$ : weight of the sample (g)

$TR$ : treated sample

$NT$ : not treated sample

## 3. Results and discussion

### 3.1. Porosimetric analysis

The physical properties of natural stones such as total effective porosity, surface area, pore size, pore geometry and pore size distribution influence the weathering phenomena and related effects. The open interconnected pore network gives a measure of the “receptivity” of a lithotype with respect to external aggressive agents but the pore size and geometry, the surface area and the pore size distribution are the really significant parameters that drive the deterioration processes due to change of state phenomena. For this reason, the mere total effective porosity of a stone and its mean pore size are only indicative but not sufficient to understand the sorption, transport, permeability, capillarity, crystallization and diffusion

processes occurring inside porous building materials that are strictly linked to the other above-mentioned parameters. The classification of porous systems following pore size and related water phenomena are reported on Fig. 1, together with pore size detection ranges covered by analytical techniques (Fitzner, B., 1994).

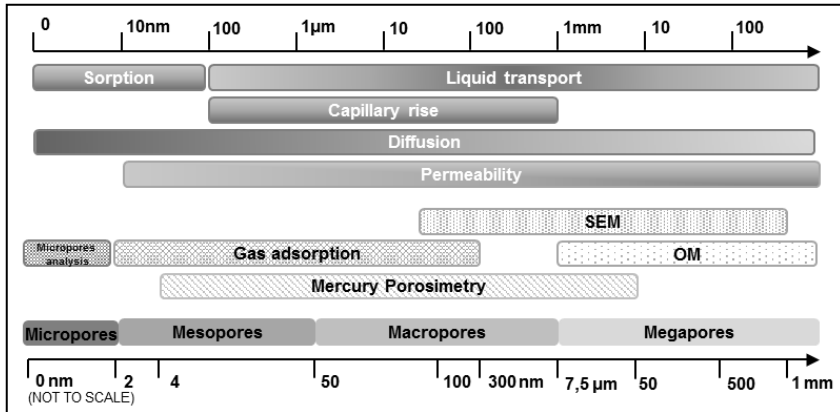


Fig. 1: Pore classification, detection analytical ranges and related water phenomena.

For this research the N<sub>2</sub>-BET (Branauer, Emmett and Teller) technique was used in order to investigate aspects related to total surface area and pore size distribution, with a focus on much fine mesopores, a range not completely covered by mercury porosimetry, in which physical sorption phenomena play a relevant role. Untreated *Globigerina* samples exhibit a surface area of 6.2 m<sup>2</sup>/g and type II isotherm-like, typical of macroporous systems, but with a weak hysteresis loop characteristic of type IV isotherm, associated with capillary condensation taking place in mesopores. The hysteresis loop is Type H3 indicating the presence of cylindrical pores or agglomerates of uniform spherical particles. Moreover, the extrapolation to a positive intercept on the adsorption axis of V<sub>a</sub>/t plot (not reported here) indicates the presence of a microporous volume (Sing K.S.W. *et al.*, 1985). Inorganic treatments induce a reduction of about 2 m<sup>2</sup>/g in the internal surface area (Tab. 2) and no significant modification in the hysteresis curves (Fig. 2). Organic treatments (with acrylic and fluorinated products) induce more dramatic changes in the internal surface area with a decrease down to around 2 m<sup>2</sup>/g (AkPU down only to 3.2 m<sup>2</sup>/g) showing a relevant occlusion of the total open porosity. The surface area after the application of ethyl silicate shows a sharp rise (up to 8.5 m<sup>2</sup>/g, about +40%) indicating the creation, by the consolidant, of a secondary porosity inside the cavities of the stone (Fig. 3). Moreover the isotherm form changes to a clear Type IV, with Type I hysteresis loop, indicating the transformation of the stone matrix into a prevalently mesoporous system. The transformation of the hysteresis loop from Type H3 to Type H1 could suggest a modification in the shape of interconnected porous network due to the deposition of the alkoxy silane gel. Mineralogy can influence the deposition mechanism by promoting acid or basic hydrolysis, the alkaline nature of the stone substrate should give rise to a soft gels film filling intergranular spaces (Wheeler, G. 2005).

Pore size distribution of treated samples in comparison with untreated ones are reported in Figures 4 and 5. Ba(OH)<sub>2</sub> and AmOx treatments cause a slight increase in all pore classes above 6 nm, a larger one in pores greater than 20 nm, suggesting a homogeneous deposition

of consolidant agglomerates reducing part of macropores into mesopores or macropores with a smaller diameter. Ca(OH)<sub>2</sub> consolidation treatment induces a small reduction in all the pore size distribution that could be explained by a better penetration capacity and deposition of nanoparticles inside the mesoporosity of stone porous network. Porosimetric distribution is completely modified by the application of SiEt on Globigerina showing a monomodal distribution with a maximum centred on the 10-12 nm pore diameter and a relevant reduction of pores between 20 nm and 80 nm. This modification can be explained by secondary porosity creation. A shift of the porosimetric distribution towards lower pore diameters was already noticed on bricks treated with SiEt: a monomodal distribution centred at  $0,4 < r < 0,5 \mu\text{m}$  was shifted to a new one centred at  $0,1 < r < 0,2 \mu\text{m}$  (Croveri P. and Appolonia L., 2002). Acrisil, Ak74 and AkCO treatments lead to similar pore distribution changes, with a decrease in all pore classes below 80 nm and a slight increase above, while for AkPU there is an evident increase of pores bigger than 20 nm, resulting from of a deposition of the product in larger macropores.

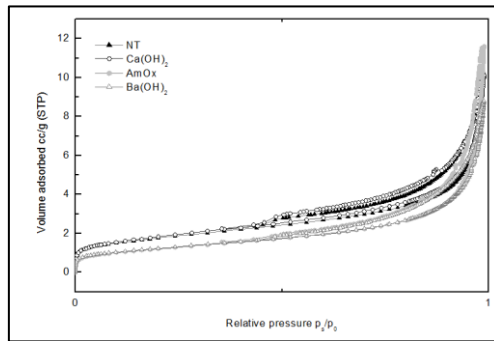


Fig. 2: Nitrogen adsorption/desorption isotherms for Globigerina Limestone.

Tab. 2: BET surface area results ( $\sigma=0.1$  estimated error 1.2%) expressed in  $\text{m}^2/\text{g}$ .

	NT	Ca(OH) <sub>2</sub>	Ba(OH) <sub>2</sub>	AmOx	SiEt	Acrisil	Ak74	AkCO	AkPU
BET	6.2	4.2	4.4	4.3	8.5	1.9	1.7	2.1	3.2

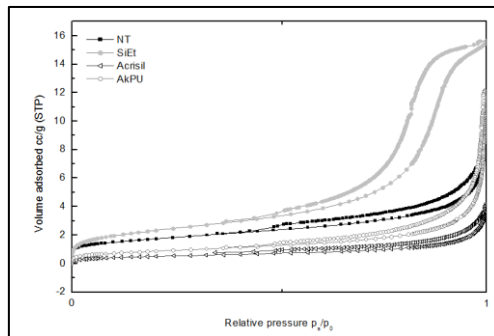


Fig. 3: Nitrogen adsorption/desorption isotherms for Globigerina Limestone.

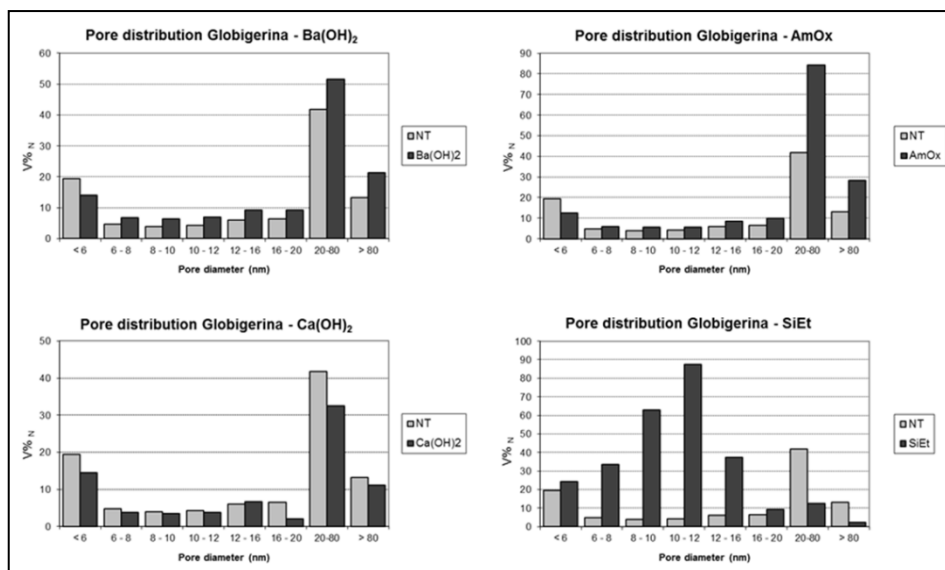


Fig. 4: Pore distribution in inorganic, SiEt treated and untreated samples of Globigerina Limestone.

### 3.2. Impact on deterioration phenomena

Changes in mesopores and small macropores (the range under investigation) potentially affect all water transport phenomena (Fig. 1). A decrease in the surface area of Globigerina Limestone can develop in parallel a dramatic change in capillarity water absorption, as in the case of organic treatments, where however the chemistry of products also plays a relevant role in the change of surface tension properties, or has slight effects as in the case of inorganic conservation treatments (Croveri *et al.* 2004). SiEt treatment impacts deserve a specific discussion since in this case the stone matrix changed from a prevalent macroporous system ( $\varnothing > 50$  nm) to a prevalent mesoporous system ( $2 < \varnothing < 50$  nm). This substantial modification of the pore network could activate, under equal environmental conditions, deterioration processes not active in the same material, when not treated. For example, a stone that does not suffer frost damage could be transformed into a freeze-thawing susceptible material. In the Maltese Islands this latter phenomenon is irrelevant, since temperatures under  $0^{\circ}\text{C}$  are generally not registered, but considering the peculiarity of the local environment it is significant to take into account aspects related to water vapour condensation and salt crystallization (Franzen and Mirwald, 2009). After treatment of Globigerina Limestone with SiEt we are moving from a system where capillary condensation occurs in most of the pores (mainly  $20 < \varnothing < 200$  nm) only when  $RH\% \geq 90\%$ , to a system where capillarity condensation takes place in most of pores (predominance of pores between 8 and 12 nm) at  $RH\% \geq 70\%$  (Colleparidi and Coppola, 1996). When environmental conditions exceed 70% RH, quite often in the Islands, the impact of treatment by SiEt is that of remarkably enhancing the quantity of water inside the porous network, potentially inducing internal stresses due to hydration - dehydration of the stone that lead to shrinking - swelling of clay components.

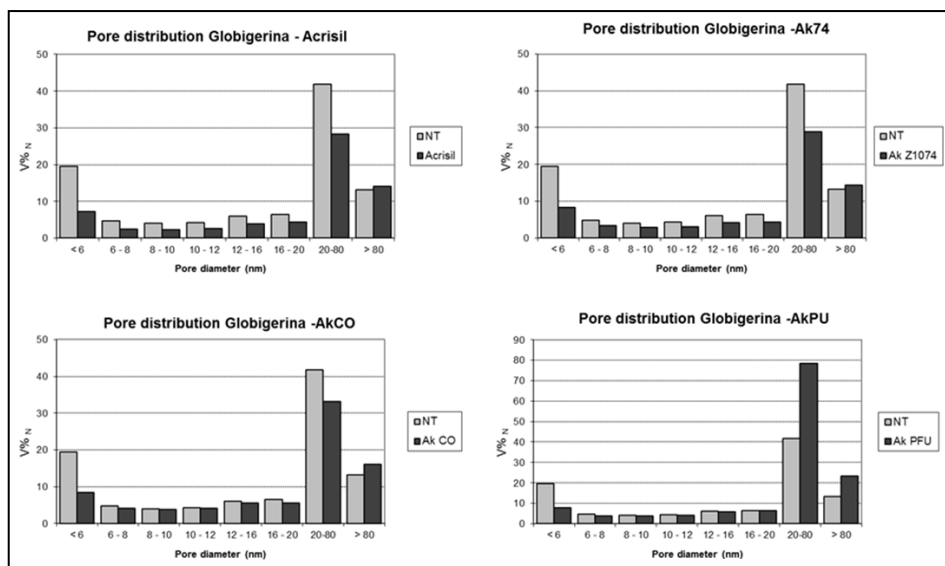


Fig. 5: Pore distribution in organic treated and untreated samples of *Globigerina* Limestone.

Water retention is associated not only with a physical factor (pore size reduction) but also with a chemical one, being the SiEt an hygroscopic material able to adsorb and retain significant water as a function of environmental thermodynamic equilibria. Moreover, in the marine environment, condensation phenomena can involve marine aerosol, inducing the transport of soluble salts inside the porosity of building materials. The enhancement of total surface area could be a negative aspect since the system offer a more extensive exchange interface to external aggressive agents (e.g. pollutant gases). The role of pore size distribution is significant also in the damage caused by salt crystallization, materials with small pores suffer from higher crystallization pressure than materials with larger pores and mineral precipitation takes place deeper beneath the stone's surface, forming subflorescences (Benavente D. *et al.*, 2004). A shift of the stone network distribution towards smaller pore diameters leads to an increase in stone decay and less resistance against salt crystallization.

#### 4. Conclusions

The main aim of conservation interventions is to change some properties of the original materials to make them more resistant towards external aggressive agents and less susceptible to decay, slowing down deterioration processes. The application of consolidant and protective products on the one part can have positive impacts on the durability of porous stone, strengthening the substrate, limiting water related phenomena (liquid transport and permeability) and mitigating the effects of physical pressure (salt crystallization, frost), but can induce modifications in the porous structure that potentially move in the opposite direction. The modification of the internal surface area and the pore size distribution of highly porous materials are relevant parameters to be investigated in order to be able to give a meaningful assessment of the effectiveness of the intervention and

to foresee and prevent any potentially dangerous effects generated by the conservation treatment itself.

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