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X-RAY COMPUTED TOMOGRAPHY AS A NON-DESTRUCTIVE TOOL FOR STONE CONSERVATION

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ABSTRACT
Lecce stone is a biocalcarenite with a very high content of calcite. It has been used for a long-time for the historical buildings in the south of Italy, especially during the Baroque period, but it is also used in the modern time. As a consequence of its high porosity (typically 40% accessible to water), it can readily take up (rain)water that can facilitate the corrosion of the rock due to the action of acidic pollution gases, such as SOx and NOx. Different kinds of organic products (Paraloid B72, fluorinated rubber or solutions of alkylalkoxysilanes oligomers) are normally applied as hydrophobic coatings (protective agents) with the aim to reduce the damage of the material.

In order to thoroughly examine the distribution of the protectives and the changes of the stone porosity due to these treatments, a number of magnified X-ray computed tomography measurements were performed, using both laboratory instruments and Synchrotron Radiation at the beamline ID19 of ESRF.

The product distribution was evaluated by porosity and other morphological parameter measurements: the results reveal that the porosity can be determined with high reproducibility and that there are significant changes of the total porosity and pores size distribution occurring as a consequence of the treatments.

INTRODUCTION
Over the past years, the conservation of historical buildings has become a more and more complex problem that depends on several factors such as the characteristics of the rock and the environmental conditions of the area where the stone artefacts or buildings are placed.

In fact, different decay phenomena caused mainly by atmospheric pollution can take place, e.g.: formation of crusts due to the action of SOx and dust [1], corrosion of the material due to the acidic atmospheric pollutants [2], formation of internal cracks due to frost-thaw cycles [3] and formation of efflorescences and subflorescences due to the dissolution/reprecipitation of salts, such as nitrates, sulphates and chlorides [4].

The internal structure of the material (porosity, pores size distribution, degree of interconnection of the pores) is a key factor that determines the behaviour of the stone and influences the processes of absorption, condensation, evaporation and migration of water: high porosity facilitates the absorption of water and thus the acceleration of the decay processes, while a high degree of pores interconnection can cause the diffusion of salt solutions inside the stone, extending the damaged areas. In all the weathering phenomena, water plays a major role [5]. For this reason, several organic products - mainly polymers - have been developed and studied in order to reduce the absorption of water and moisture and, as a consequence, to preserve the material [6]. After the application of the protective product, the surface must be completely water repellent, but the petrophysical properties of the material, such as the permeability to the water vapour, should not change drastically, in order to avoid the damages deriving from the entrapment of liquid water inside the stone.

As the performances of different conservation products - especially in relation to the prevention of the damages due to the atmospheric pollutants - depend mainly on their penetration depth and distribution inside the pores, the determination of these parameters is crucial for the evaluation of the treatment efficacy.

X-ray micro tomography (μ-CT) is a non-destructive technique suitable for this purpose. It is based on a set of X-ray radiographs of the sample acquired at different rotation angles: each radiograph is a map of the attenuation of the X-ray photons inside the sample; from this dataset it is possible to reconstruct mathematically the transversal sections of the specimen. Because it is a non-destructive technique, the same sample can be analysed before and after treatment or artificial ageing, in order to monitor the changes of the stone that may occur [7].

The same types of tomographic investigation can be performed using Synchrotron Radiation (SR-CT), which allows to obtain images with higher quality and to improve the contrast between stone and polymers.

The aims of the current experiments are: a) to evaluate the performance and the potentialities of μ-CT instrument in stone conservation, b) to evaluate the effects of conservation treatments on stone materials, monitoring the changes of the rocks' characteristics, such as porosity, caused by conservation treatments and c) to explore the applicability of Synchrotron Radiation tomography (SR-CT) for visualising the protective products inside the pores and studying their distribution.

MATERIALS AND METHODS

For this research, a biocalcarenite (Lecce stone) was chosen. This rock takes its name from the city of Lecce in the south of Italy. It is, however, an extensively used material in the entire Salento region. It has been used for a long time, especially during the Baroque period, to cover the façades of the most important and beautiful buildings of that area (e.g. the Basilica of Santa Croce in Lecce) as well as for sculptures. Nowadays, it is employed for the realisation of decorative objects.

A petrographic examination of Lecce Stone reveals that it is made of a grain mixture of microfossils, fossil fragments and shells, with dimensions ranging between 100 and 200 μm, incorporated into the calcitic cement. Calcium carbonate is the basic component, with a total of 93-97%, while small amounts of granules of quartz, glauconite, feldspars and clay minerals re present. The total open porosity determined by a Quanta Chrome helium Penta-Pycnometer is 47.4±1.2%, whereas meso porosity (i.e. 3.5×10^{-3} – 150 μm radius), determined by means of a Thermofinnigan mercury intrusion porosimeter, is 35.8±2.1%. The porosity accessible to water, measured by weighing the specimen before and after saturation with water, is 39.0±0.2%.

Two polymeric conservation products have been used to treat the stone samples:

- Paraloid B72 (PB 72) which is poly(ethyl methacrylate-co-methyl acrylate) (70/30) with an average molecular weight (MW) of 91000 amu

- Fluoroelastomer (NH) which is poly(hexafluoropropene-co-vinylidenefluoride), MW = 350000 amu.

Both the selected protective products are widely used for stone conservation and they were applied as acetone solution with a concentration of 2% (w/w) for PB72 and 1% (w/w) for NH by impregnation under reduced pressure (10 mmHg).

μ-CT measurements

For the μ-CT measurements, a SkyScan 1172 system was used. The x-ray micro focus tube (tungsten reflection target) of the μ-CT system was set at a voltage of 100 kV and a current of 100 μA, applying a filter (Cu 0.038 mm + Al 1 mm), in order to obtain a better contrast and to prevent beam hardening artefacts. Radiographs, with isotropic resolution of 2.6 μm in terms of pixel/voxel size, were acquired by means of a CCD camera of 4000 x 2096 pixels binned to 2000 x 1048. frame averaging of 4 and a rotation step of 0.4° were chosen to minimize the noise, covering a view of 180°.

The projections were processed using a modified Feldkamp cone-beam algorithm and a stack of 2D cross-section images of the samples were obtained [8].

The data set was analysed with the “CTAn” software package in order to create a complete 3D representation of the internal microstructure of the stone and to calculate the main important morphometric parameters, characterizing the samples:

- Porosity, as a percentage of the empty spaces on the volume of interest (VOI)
- Pore size distribution
- Wall thickness distribution (i.e. the distribution of the stone thickness between two pores) and wall thickness average, calculated as the weighted average of the wall dimensions

All the parameters of the same sample were calculated in 3D and compared before and after the treatment in order to study the changes of the stone structure and properties induced by the application of the conservation products.

SR-CT experiments at ESRF

The experiments of SR-CT have been performed at ID 19, one of the beamlines of ESRF dedicated to x-ray imaging [9]

Lecce stone samples (1 x 1 x 10 mm^3) untreated and treated with conservation products (PB 72), have been analysed with the aim of investigating, at micro-scale, the polymer distribution. The samples have been mounted on a rotation stage which also allows the adjustment of the rotation axis, and a FRELON (Fast Readout Low Noise) camera 2048 x 2048 has been used as a detector. This is a 14-bit depth resolution CCD camera developed at ESRF, which allows a fast acquisition of radiographs, a good quality of the images and a high magnification thanks to the optics system.

The samples have been scanned with a beam energy of 19 keV which allows a transmission of about 30%. For each tomography scan, 1500 projections over a 180° rotation (rotation step = 0.12°) have been acquired with a pixel size of 700 nm. These conditions provide a good balance between quality of the reconstructed images and scanning time (one scan takes about 20 minutes).

The reconstructed images have been qualitatively evaluated to highlight the presence of the conservation treatments and the manner in which they coat the stone pore walls.

RESULTS AND DISCUSSION

In order to exclude the fact that variations of morphological parameters calculated by μ-CT data are due to the instrumental precision or to the manipulation of the specimens, the repeatability of the measurements has been tested by scanning the same sample five times and calculating the porosity values. The scans have been performed by removing/repositioning the sample from the scanner every time.

The variations values in Tab. 1 show that the porosity values range from 38.1 % to 37.1 %, thus the difference between the maximum and minimum value is 1%. Therefore, it is possible to monitor the porosity changes of samples induced by conservation treatments and/or ageing, but it should be taken into account that variations within 1% may be caused by measurement uncertainty and only changes higher than 1% are significant.

No. Scan	**1**	**2**	**3**	**4**	**5**	**Average**
Porosity (%)	38.1	37.5	37.1	37.6	37.5	37.6±0.4

Tab. 1 - Repeatability test: porosity values of the same sample calculated from five different μ-CT measurements

Porosity values obtained before and after treatment with PB 72 are presented in Tab.2. The two averages, before (39.4±1.3 %) and after (36.3±1.6 %) the polymer application, were compared through a t-test, in order to determine whether the protective product has caused significant changes at a given level of significance, α. The t-test, with a statistical probability of 99% (α = 0.01), reveals that the two averages are significantly different and we can conclude that PB 72 caused a decrease in porosity of 3.1±1.1.

	Samples treated with PB 72							
	1	2	3	4	5	6	7	Average
Porosity Before Treatment (%)	38.5	38.6	41.0	38.1	38.9	39.5	41.3	39.4±1.3
Porosity After Treatment (%)	37.1	35.1	36.4	33.9	36.3	36.7	38.8	36.3±1.6
Difference Before-After (%)	1.4	3.5	4.6	4.2	2.6	2.8	2.5	3.1±1.1

Tab. 2 – Porosity values (%) and standard deviations of samples before and after treatment with PB 72

The porosity is not the only morphological parameter that changes. The wall thickness distribution graph shown in Figure 1 shows that there is a small decrease in the thinner walls (arrow A) and a slight increase in the thicker ones (arrow B) after the treatment. By forming a protective film along the walls of the pores, PB 72 has probably induced a wall-thickening effect. These slight changes have been noted also in the average wall thickness, since the value after treatment increased from 21 μm to 23 μm: again the t-test reveals that the two averages of the wall thickness are significantly different.

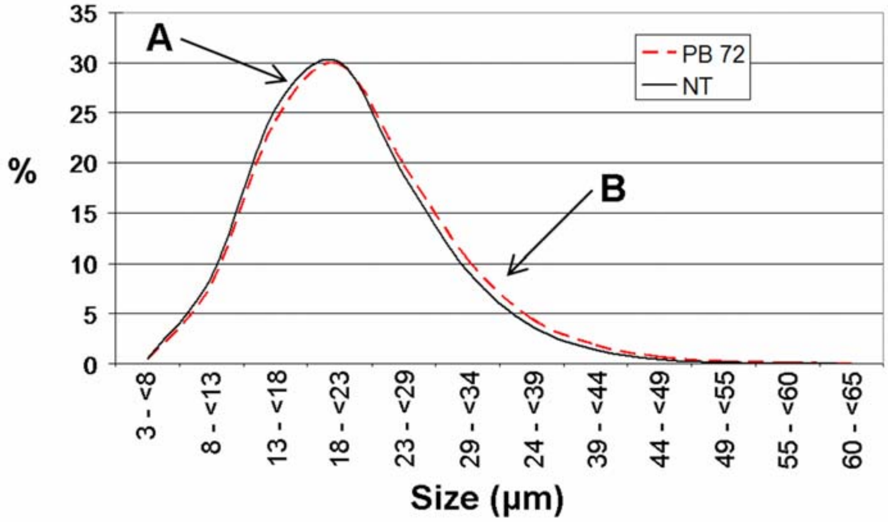

Fig. 1 - Wall thickness distribution of Lecce stone samples untreated (continuous line) and treated with PB 72 (broken line). The profiles were calculated on an average of 7 samples

Unexpectedly, only small differences have been found in the pore size distribution before and after the treatment. Since the pore size is calculated as the diameter of the largest sphere that can be inscribed in the cavities, it is possible that the polymer in some cases fills small cavities and irregularities leading to an increase of the wall thickness, without changing the pore dimension. Indeed PB 72 provides the stone with good water repellence, without drastically changing the natural characteristics of Lecce stone, so harmful effects due to the occlusion of the open porosity and/or to the formation of a continuous film on the surface of the artefacts should be avoided.

The values of porosity obtained before and after treatment with NH are presented in Tab.3. The two averages obtained before (39.6±1.2 %) and after (31.2±1.8 %) the application of the polymer, were compared again through a t-test: the two averages are significantly different, the decrease in porosity caused by NH is estimated to be 8.4±1.0 %.

	Samples treated with NH							
	8	9	10	11	12	13	14	Average
Porosity Before Treatment (%)	39.7	37.7	39.6	40.9	39.9	38.4	41.1	39.6±1.2
Porosity After Treatment (%)	33.3	28.9	30.3	32.4	31.7	29.1	32.9	31.2±1.8
Difference Before-After (%)	6.4	8.8	9.3	8.5	8.2	9.3	8.2	8.4±1.0

Tab. 3 - Porosity values (%) and standard deviations of samples before and after treatment with NH

The wall thickness distribution graph (Fig. 2) shows a strong decrease in the amount of the thinner walls (arrow A) and a considerable increase in the thicker ones (arrow B). The NH treatment has induced a thickening effect due to the coating of the pores and the grains of the rock. The same behavior has not been noticed in pore size distribution, where no appreciable changes of untreated vs. treated have been observed. It is possible that the product application has changed the wall thickness distribution and the total porosity, inducing a very small variation of the distribution of the pores dimension, as in the case of the treatment with PB 72. This small variation, associated with the appreciable decrease in porosity, also suggests that part of the cavities could be completely filled by the polymer.

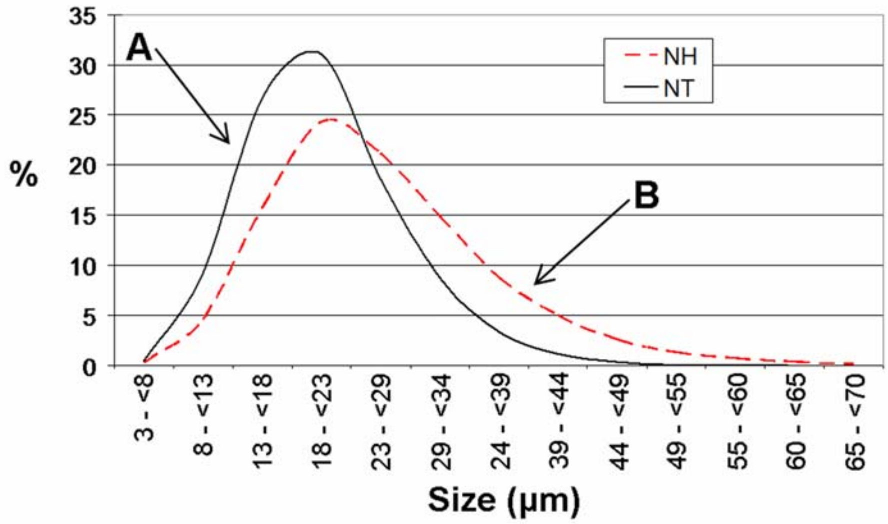

Fig. 2 – Wall thickness distribution of Set3 untreated (continuous line) and treated with NH (broken line). The profile shows the decrease of the thinner walls (A) and the increase of the thicker ones (B)

The natural average wall thickness has increased from 21 µm to 26 µm after the application of the polymer.

At the spatial resolution provided by the µ-CT scans (2.6 µm) it is not possible to visualise directly the polymer in the reconstructed images. Moreover, the product fills pores too small to be detected and creates very thin films around the grains of the stone, and they are therefore very difficult to distinguish also because of the low contrast between the water repellents and the stone.

The results obtained with the lab system can be improved by performing SR-CT. The quality and the monochromaticity of the x-rays, produced by the synchrotron, significantly enhance the contrast between stone and protective products in the reconstructed images, so that polymers become visible in Lecce stone samples of 1 x 1 x 10 mm^3 dimensions, treated with Paraloid B 72 scanned at ID19 of ESRF (Fig.3).

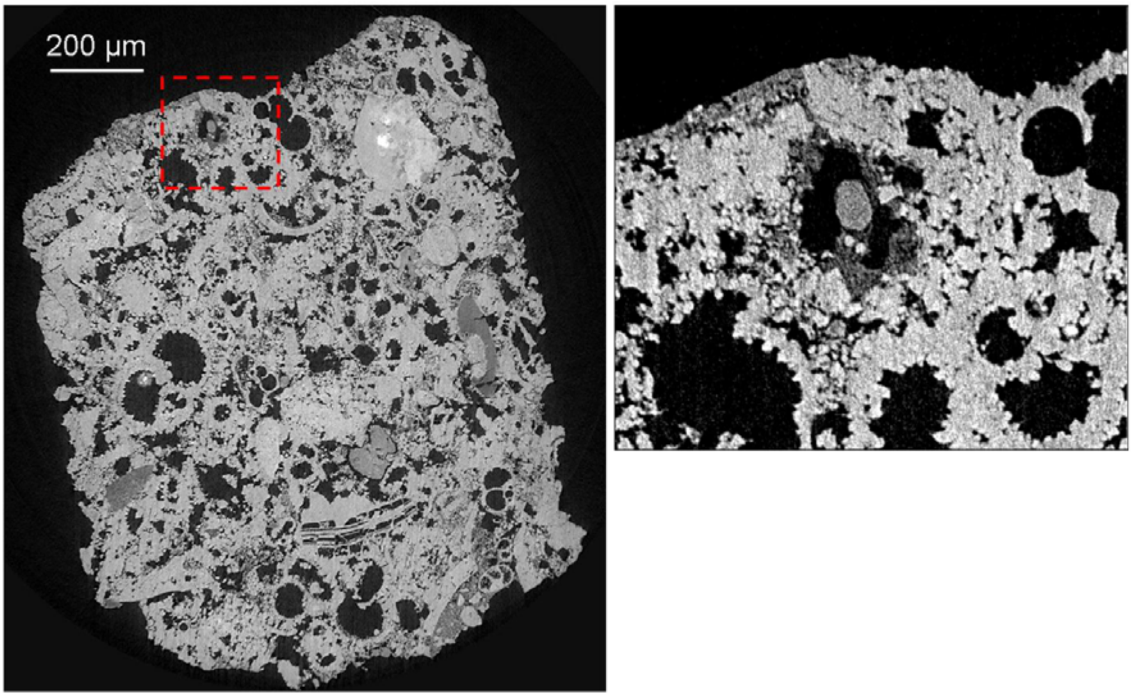

Fig. 3 – Cross section of Lecce stone treated with PB 72, obtained by means of SR-CT

The protective products are distributed in thin films around the grains of Lecce stone and on the walls of the pores. On the other hand, there are areas in the samples where the polymer is not present. This may be due to the small size of the specimens (1 mm), so that the capillary suction and the treatment uptake are rather limited. Despite the application by impregnation under reduced pressure, the amount of product deposited in the stone structure seems to be quite modest.

CONCLUSIONS

X-ray μ-CT demonstrated to be a powerful tool for the investigation of the internal structure of building materials and more in general for stone conservation. If compared with other methods, the main advantages of μ-CT are the simple preparation of the sample and the non-destructivity of the analysis. This allows to compare the characteristics of the same samples at different steps, e.g. before and after treatment or ageing.

The polymer distribution in the internal structure of the rock is influenced by the physical and chemical properties of the products (molecular weight and chemical affinity with stone). In fact, NH, having high molecular weight and low affinity with calcarenites, causes a significant decrease in porosity with partial or complete blockage of some pores and non-homogeneous distribution inside the stone. On the other hand, PB 72, having lower molecular weight and a higher affinity for stone, causes small changes to the natural properties of Lecce stone with moderate variation of the pore size and wall thickness distribution, suggesting a homogenous polymer distribution in the stone structure.

The results also show that SR-CT can be successfully used to visualize conservation treatments, their distribution and the manner in which they coat the pores. The high resolution and the possibility to analyze small samples make SR-CT a non-destructive technique suitable for the investigation of not only laboratory specimens, but also fragments taken from historical buildings' façades.

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ENDNOTES

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