X-ray microtomography as a non-destructive tool for stone characterization in a conservation study

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Abstract – Calcareous stones such as Lecce stones have a high porosity which results in a readily uptake of rainwater. Due to the atmospheric pollutants dissolved in the water these stones, used in a lot of historical buildings, are constantly under attack which leads to a decay of the stone. Different kind of organic hydrophobic products such as Paraloid B72 and fluorinated rubber are often applied as protectives with the aim to reduce the corrosion of the material. In order to study the manner in which these treatment products fill the pores a desktop X-ray microtomography system was used. This technique allows the 3D investigation of the internal structure of the stone in a non-destructive way. In this research morphological parameters such as the total porosity, pore size distribution, surface-to-volume ratio and structure model index were calculated before and after treatment in order to evaluate the changes induced by the polymer application.

Keywords: X-ray micro-CT, Lecce stone characterization, conservation products

1 Introduction

Water plays an important role in the decay process of stones [1]. Not only the daily and seasonal thermo-hygrometric cycles are important but also the dissolved atmospheric pollutants in the water have an aggressive contribution to this process. This is true especially in urban areas where emission sources like traffic and industry are located. These continuous chemical and physical changes will affect Cultural Heritage materials depending on the establishment of a dynamic equilibrium with the environment in which they are situated. In particular different phenomena can take place such as the formation of black crusts, corrosion of the material, internal cracks…

A biocalcarenite such as Lecce stone has a very high content of calcite and a high porosity. With 40% of the pores accessible to water the uptake of rainwater and thus also of acidic pollution gases such as NO_x and SO_x leading to the acceleration of the corrosion of the stone is facilitated. In general calcareous stones containing calcite and dolomite are more sensitive to the chemical action of acidic pollutants in comparison with silicate rocks. Furthermore Lecce stones are typical construction materials which have been used for long-time in historical buildings in the South of Italy especially during the Baroque period. Nowadays it is still largely used as a material for decorative objects.

In order to conserve these works of art different kinds of hydrophobic organic products are applied on the surface of the restored artefacts. Since the efficacy of the treatments depends mostly on the penetration depth and the distribution of the products in the pores, porosity and internal structure of the stone material were mainly investigated in this research. Furthermore it is of interest to study the materials before and after the treatment which means that a non-destructive method is needed. For this X-ray computed tomography (CT) was applied.

X-ray CT is a relative new technique developed in the late 1970's, which enables the non-destructive visualisation of the internal structure of objects. These first, mainly medical, CT scanners had a pixel resolution in the order of 1mm. In the 80's, after some technological advances towards micro-focus X-ray sources and high-tech detection systems, it was possible to develop a micro-CT system with nowadays a pixel resolution 1000 times better than the medical CT scanners [2,3].

The technique of X-ray (micro)-CT is based on the interaction of X-rays with matter. When X-rays pass through an object they will be attenuated in a way depending on the density and atomic number of the object under investigation and of the used X-ray energies. By using projection images (cf. roentgen photos) obtained from different angles a reconstruction can be made of a virtual slice through the object. When different consecutive slices are reconstructed a 3D visualisation can be obtained.

The aim of the present experiments is to evaluate the performance and the potentials of the high resolution µCT technique on the Lecce stone samples before and after treatment.

2 Methods

2.1 Preparation of the samples

For this study Lecce stone was chosen. This bioclastic limestone has a grain size distribution between 100 and 200 µm. Its total open porosity determined by a Quanta Chrome helium Penta-Pycnometer is 47.4 ± 1.2%, whereas the meso-porosity determined by the Thermofinnigan mercury intrusion porosimeter is 36 ± 2%. The porosity accessible to water is measured by weighing the specimen before and after saturation with water and gives a value of 39.0 ± 0.2%. The content of calcite determined with X-ray diffraction is 93-97% [1].

From a bigger untreated block, five samples were cut to a size of $3x3x3mm^3$, suitable for the micro-CT measurements, and used for the basic characterization of the rock. Two of them were treated each with one of the selected protective products widely used for stone conservation:

1) Paraloid B72 (PB 72): poly(ethyl methacrylate-*co*-methyl acrylate) (70/30), average molecular weight (M_W) = 91 000amu, glass transition temperature (T_g) = 43°C. It was applied as acetone solution (2%, w/w);
2) Fluoroelastomer (NH): poly(hexafluoropropene-*co*-vinylidenefluoride), M_W = 350 000amu, T_g = -18°C. It was applied as acetone solution (1%, w/w).

The treatments with PB72 and NH were performed by impregnation under reduced pressure (10mm Hg): the specimens were put in a Schlenk flask connected to a membrane vacuum pump for 2h in order to eliminate air and moisture inside the pores. Afterwards, the treatment solution was added using an addition-funnel until the sample was completely immersed. After 20h the samples were drawn out and dried at room temperature.

2.2 Micro-CT system

For the microtomography measurements a SkyScan 1172 was used. This is a high resolution desktop X-ray micro-CT system with a closed X-ray micro-focus tube. The maximum peak voltage of this source is 100kV with a maximum power of 10W. It has a Tungsten reflection target and a focal spot size of 5µm. The detection system consists of a gadox (Gd_2O_2S) scintillator with a 2:1 fibre optics coupling to a 4000 x 2096 large format 12-bit cooled CCD camera.

The sample was placed on a sample holder between the X-ray source and detector. As a consequence of the cone beam of the source the distance of the sample to the source determines the magnification of the system. This magnification will be set so that the sample stays within the field of view of the detector for the full rotation cycle. In other words for doing micro-CT experiments the diameter of the sample is of utmost importance for reaching a good resolution. By using camera binning, i.e. 2 by 2 pixels taken together giving 2000 pixels on a detector row instead of 4000, an isotropic pixel resolution of 2.5 µm was obtained for this dimension of samples.

Due to the relatively high absorption of the Lecce stone the low energy part of the X-ray spectrum was cut-off using a filter of 0.038mm copper and 1mm aluminium. In this way a better contrast was obtained and the beam hardening artefact was reduced. A frame averaging of 4 and a rotation step of 0.4° were chosen to minimize the noise, covering a view of 180°.

After the acquisition of the projection images the reconstruction was done using a modified Feldkamp cone-beam algorithm [4]. Finally the 2D cross-sectional images of the sample were obtained in consecutive slices throughout the stone.

2.3 Morphological parameter analysis

The obtained 3D data set was processed and analysed with the "CTAn" software package [5] in order to create a complete 3D representation of the internal microstructure of the stone. After selecting a region of interest (ROI) a global thresholding was performed creating binary images of the pore network. From these images it was possible to calculate the main important morphometric parameters of the samples:

- Porosity, as a percentage of the enclosed empty spaces on the volume of interest (VOI)
- Pore size distribution, calculated with a sphere fitting method [6].
- Surface-to-volume ratio, which gives an idea of the complexity of the internal structures.
- Structure model index (SMI), giving an estimation of the average shape of the pores (0 = ideal plate, 3 = cylinder and 4 = sphere).

Note that with 3D image analysis by micro-CT a true 3D thickness can be measured. This is determined as an average of the local thickness at each voxel representing solid, in this case i.e. the pore network and thus the pore sizes. Local thickness for a point in a solid is defined by Hildebrand and Ruegsegger [6] as the diameter of a sphere which fulfils two conditions: first of all the sphere encloses the point (but the point is not necessarily the centre of the sphere); secondly the sphere is entirely bounded within the solid surfaces. In other words a complex object like the pore network of the stone can be characterized by a single mean value or by a distribution of thicknesses (cf. pore sizes).

These parameters were determined on a set of untreated samples in order to characterize the stone. The porosity was calculated before and after the treatment in order to study the changes due to the application of the protective product.

3 Results

After the reconstruction a stack of transversal 2-dimensional virtual slices through the sample is obtained. One of these slices is shown in Figure 1.

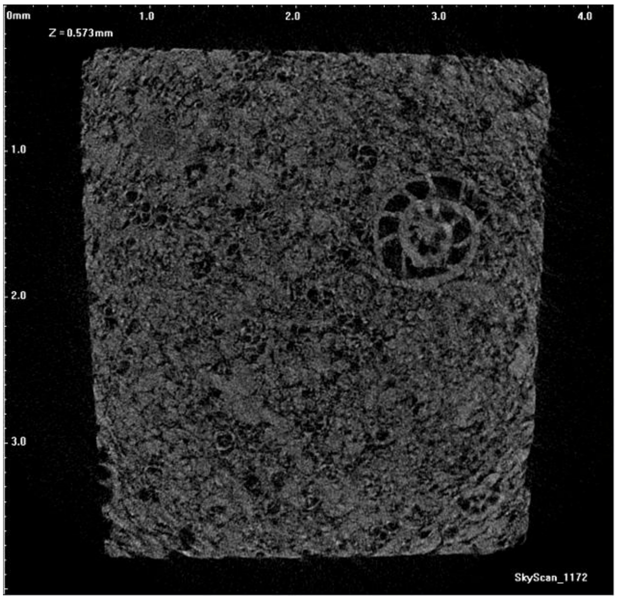

Figure 1: Reconstructed cross-section of a Lecce stone sample scanned with micro-CT at a pixel size of 2.5µm.

Since this represents a 3D volume, these slices can also be visualized in 3 orthogonal directions called: transversal, coronal and sagittal slices. These are shown in Figure 2 where a zoom on the reconstructed image is seen. The names are corresponding with the images in clockwise direction, knowing that the bigger image represents the original transversal slice. The coronal and sagittal cuts are made through the shell in the middle of the image.

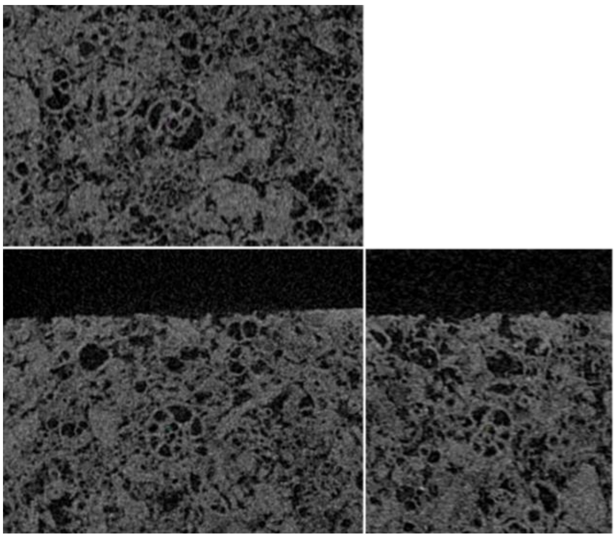

Figure 2: A zoom of a reconstructed cross-section of a Lecce stone, including the coronal and sagittal views made through the shell in the middle of the transversal image.

When selecting the pore network for the binary images it is possible to create a 3D model by volume rendering. This model can be used for visualisation, rotation, translation, flying-through the object, making avi-files… In Figure 3 the complex 3D network of the pores of the Lecce stone is shown.

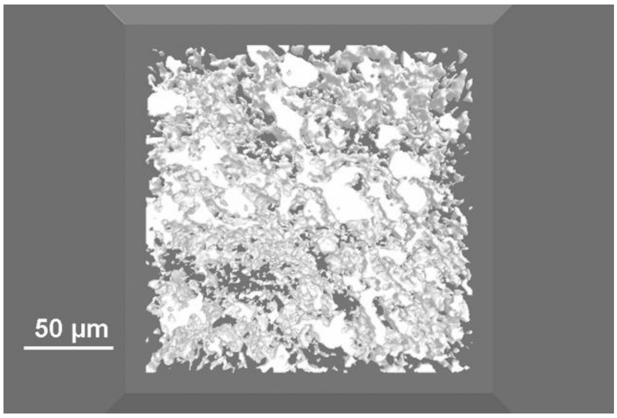

Figure 3: 3D rendering of the pore network of a Lecce stone.

Not only the visualisation is a helpful tool but also quantification is necessary. For this different parameters are calculated from the 3D data set. The five untreated samples were used for obtaining the following parameters: the average surface-to-volume ratio of the pores was calculated as 275mm^{-1}; the pore size distribution calculated with the sphere fitting method is shown in Figure 4; the structure model index or SMI value was calculated as 1.9.

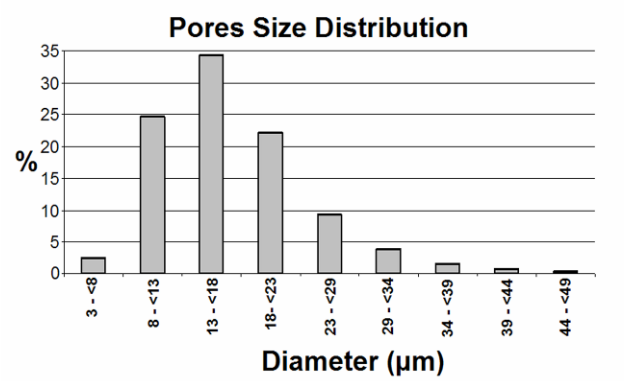

Figure 4: Pore size distribution calculated with the sphere fitting method of Hildebrand and Ruegsegger [6]

In order to test the repeatability and to measure the errors coming from the system, one of the samples was scanned 5 times. The acquisition, reconstruction and analysis values such as the ROI and threshold values were kept the same. The results of the porosity can be found in Table 1.

Table 1: Repeatability test

Scan Number	*Porosity in %*
1	38.1
2	37.5
3	37.1
4	37.6
5	37.5
Average	*37.6 ± 0.4*

Finally the porosity was calculated before and after the treatments with PB72 and NH. The results can be found in Table 2.

Table 2: Porosity calculated before and after the treatment

Product	*Before*	*After*	*Decrease*
PB72	33.1%	29.5%	*3.6%*
NH	29.4%	26.5%	*2.9%*

4 Discussion

The 2D reconstructed cross-sections, shown in Figure 1 and 2, confirm that Lecce stone has a very complex internal structure, as suggested by the environmental scanning electron microscopy (ESEM) image of the surface which can be seen in Figure 5.

Figure 5: Environmental scanning electron microscopy (ESEM) image of the surface of a Lecce stone sample

Several different inclusions such as shells with different shapes and sizes (from a few µm up to 1mm, foraminifera in Figure 1) can be clearly distinguished. Moreover, the calculated average surface-to-volume ratio of the pores ($275mm^{-1}$) indicates a very intricate shape of the pores. This last result seems to be confirmed by a 3D rendering of a small portion of the pores network (Figure 3), which gives an idea of the complexity and interconnectivity of the internal structure. The pore size distribution (Figure 4) shows that almost 90% of the pores range from 8 to 29µm. The calculated Structure Model Index (SMI) is 1.9 which means that the average shape of the pores is supposed to be between a plate (SMI = 0) and a cylinder (SMI = 3), i.e. similar to a cylinder but flattened. This is an important result, because all the other techniques allow us to investigate the pores size distribution, but not their real shape.

Five Lecce stone samples were analyzed and the results of the calculated parameters as discussed above were similar for all the specimens and thus representative for the whole block of stone, except for the porosity. In fact these values change from sample to sample as the results range from 28% to 35%. This may be due to the limited dimension of the samples: for sedimentary lithotype, like Lecce stone, inhomogeneities in porosity are normal, even if the samples come from the same block of rock.

In order to exclude that these variations are due to the instrumental accuracy or to the manipulation of the specimens, the repeatability of the measurements was tested: the variations of the porosity values, calculated from 5 different tomography scans of the same sample, were less than 1% (Table 1). This allows monitoring the porosity of the samples in order to study the changes on this parameter that may occur due to the protective treatment, taking into account that variations within 1% can be due to the analysis and only changes higher than 1% are significant.

With this knowledge the porosity was calculated before and after treatment (Table 2**).** The first sample had a porosity before treatment of 33.1%. After treatment with PB72 its porosity decreased 3.6%. The same procedure was followed for the second sample (porosity = 29.4%), treated with NH, causing a decrease in porosity of 2.9%. In both cases the variation of the porosity due to the conservation treatments is significant, but very small. The treatments give very high water repellence to the stone, as reported in [7], but they do not drastically change its natural porosity. On the other hand, it should be also considered that the protective products are probably distributed in very thin films around the grains of the stone and on the walls of the pores, and, as they are organic polymers, they have a low X-ray attenuation coefficient, in comparison to the rock. For these reasons the decreases in porosity calculated from the µCT images may be underestimated.

5 Conclusions

X-ray micro-CT demonstrated to be a powerful tool for the investigation of the internal structure of building materials. The reconstructed cross-sections and 3D rendering of the pores network are able to show, qualitatively the shape and quantitatively the dimension of the pores. Moreover, the data processing allows calculating different morphological parameters useful to characterize the stone. Because µCT is a non-destructive technique and it has a high repeatability, the samples can be monitored during the conservation treatments following the changes in porosity of the specimens that may occur.

As a conclusion of this preliminary research, the micro-CT technique is a valid support for evaluating the penetration depth and the distribution of organic polymers used as stone consolidant and protective agents. Undoubtedly, further studies will be necessary, in particular, a statistical treatment of the data in order to estimate the errors on the calculated 3D parameters.

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