X-ray micro-CT used for the localization of water repellents and consolidants inside natural building stones

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Abstract

Natural stones used in monuments have to deal sooner or later with weathering. The desire to preserve cultural heritage created a wide variety of products to reduce the rate of stone decay and to strengthen decayed stone. The ability of these water repellents and consolidants to penetrate inside natural building stones is one of the main factors controlling their performance. The determination of this penetration depth is crucial for the application of conservation products. Because the impregnation depth also depends on the characteristics of the material itself, such as total porosity and pore size distribution, these should be considered when restoration is planned. X-ray micro-computed tomography (μCT) was used to determine the impregnation depth of water repellents and consolidants. 3D information about the total porosity and the pore size distribution was obtained with the combination of μCT and home-made 3D software. This experiment should provide a basic step for extra advice on the suitability of products for the treatment of a particular rock type.

Keywords: Natural building stones; Water repellents; Consolidants; Porosity; Impregnation depth; X-ray micro-computed tomography

1. Introduction

Natural building stones used in monuments have to deal sooner or later with the different physical, chemical and biological weathering actions. The decay of stone is a complex process that generally starts with alteration processes due to the synergetic action of rain, wind, sunlight and freezing/thawing cycles [1]. All these weathering types are connected with the presence of water and the pore system of the stone. Some well-known moisture-related damages are frost action, expansive chemical reactions and biological degradation [2]. Frost action, which can be a disruptive factor, results in the combination of different factors, such as the volumetric expansion from water to the ice phase, the degree of water saturation of the pore system and the critical pore size distribution. The solvent action of water and its dissolved impurities, such as sulfate, carbon dioxide...
and nitrate, are largely responsible for the chemical attack on stone [3]. The decay rates of materials are related to the type of stone, their treatment and the atmospheric conditions [4].

The growth in the renovation and the maintenance activities of old buildings has largely contributed to the success of water repellents and consolidants. The desire to preserve cultural heritage created a wide variety of products to reduce the rate of stone decay and to strengthen decayed stone. The greatest difficulty however is the selection of the most appropriate product out of this wide range of products [5].

Water repellents are intended to reduce the moisture-related damage risks and to ensure or prolong the required service life of monuments [2,6]. Water repellents also have the characteristic to ameliorate the resistance against pollution of the façades. Although water repellents can be very useful, sometimes they can be more harmful for the stone, especially when they alter some petrophysical parameters of the material [5]. When water repellents are applied, it is important that the whole treated region is totally water repellent to prevent incoming water, being captured behind the treated water repellent layer. In this way, the pore size distribution of the stone is of great importance. For pores larger than 0.3 mm, the water repellent will not work sufficiently enough to repel water [6,7]. A good impregnation depth is also favorable for the durability of the treatment, but there is no direct relation between the impregnation depth and the capabilities of the water repellents [6]. The impregnation depth of water repellents can vary between a few hundreds of a millimetre and a few centimetres [6]. On the other hand, the relation between the capillarity of the stone and the working capability of the water repellent is very important.

Consolidants are widely used in restoration and conservation interventions as a means of imparting the structural strength of a stone, which has been deteriorating and is disintegrating. Consolidation is an artificial way of repairing the bonds that normally hold the stone together. A good consolidant should meet performance requirements concerning durability, depth of penetration, effect on stone porosity, effect on moisture transfer, compatibility with stone and effect on appearance [8]. A universal consolidant does not exist because many of these factors will vary to some extent from stone to stone [8]. When consolidation is planned, each stone structure should be considered as a unique problem. A very important requirement of a consolidant is the fact that it can impregnate the stone and impart its strength. There is a long way between the start of the consolidation, where the consolidant has a liquid form and the end, where it turns out to be solid. The penetration of the consolidant will depend on factors like the viscosity of the liquid and the size of the pores. Young et al. [9] and Price [10] mention that a treatment should penetrate the stone to at least 25 mm or to the depth of stone deterioration. This should result in a gradual transition in the thermal and mechanical properties from the exterior treated surface to the inner layer of the untreated stone [8].

Porosity influences to a large extend the action of water repellents and consolidating products. Because the pore size controls the capillary action, water and other liquids can be differently absorbed on stone types with different pore size distributions. This is the main reason why a certain product can work excellently for a certain type of stone but can be very harmful for a different stone type [5]. The surface tension of a liquid, its viscosity and the pore size determine the weathering rate and the penetration depth inside a stone [8]. The most important characteristics that have an influence on liquid transport in a porous medium are porosity, numeric density, pore shape and pore connectivity [11].

Determining the penetration depth of water repellents and consolidants is crucial if the application of conservation products is planned. Existing test methods for measuring penetration depth are water droplet absorption time (only for water-repellent treatments), visual observation of color changes on wetting and drying (mainly for water-repellent treatments), water vapor permeability and strength tests [9]. These tests are very superficial and operate at a different magnification level than X-ray micro-computed tomography (μCT). To assess the penetration depth and the effectiveness of a certain restoration product, μCT technology can be applied together with traditional techniques. μCT is similar to the conventional medical scanners, with the major advantage that it provides images with a higher spatial resolution. An X-ray micro-computed tomograph contains basically a fixed X-ray source and detector array while the
object is rotating. At discrete angles, the source detector configuration measures a one-dimensional projection of X-ray attenuation coefficients. These attenuation coefficients in various directions are processed to produce 2D cross-sectional images. Based on these 2D images, 3D reconstructions can be created. When an X-ray beam passes through an object, beam intensity decreases due to absorption and scattering. The amount of this attenuation depends on both electron density $\rho$ and atomic number $Z$ and on the photon energy spectrum of the X-ray beam. Beer’s law relates the intensity ($I$) of X-ray photons passing through the object with thickness $h$, with the incoming intensity ($I_0$) and the attenuation coefficient ($\mu$) of the object:

$$I = I_0 e^{(-\mu h)}$$

(1)

If several absorbing materials are presented, this relationship is summarized by:

$$I = I_0 e^{(-\sum_{i}^{n}\mu_i h_i)}$$

(2)

with index $i$ referring to every type of material occurring in the X-ray beam. For equivalent X-ray energy, a more dense material (e.g., the rock matrix) will attenuate the beam more than a less dense material (e.g., gas- or liquid-filled pore). This property makes it possible to distinguish material from pores and liquids. Another major advantage of this technique is that it provides non-destructive 3D visualization and characterization of the objects [12]. This enables to visualize the situation inside the stone before and after treatment. When the products such as water repellents and consolidants have a different density or atomic number than the stone material itself, their localization inside the stone will be clearly visible.

Porosity, pore size distribution, pore geometry and permeability are important material characteristics in the investigation of weathering and conservation phenomena of natural building stones [13]. Porosity is a basic feature of a rock, whereas permeability depends on the effective porosity, the shape and size of the pores and their interconnections (pore throats) and on the properties of the fluid itself (i.e. capillary force) [14]. Several methods exist to determine porosity. Each method, such as water absorption, mercury intrusion porosimetry (MIP), $N_2$-absorption, NMR microscopy and image analysis of microscopical thin sections, presents certain limits and disadvantages [14,15]. Because of the complexity of the pore structures in natural building stones, measuring the total porosity and the pore size distribution can be difficult [16]. Petrographical image analysis of thin sections is a method widely used for acquiring data on pore geometry [17–20]. When analyzing thin sections, account must be taken that the pore size distribution results determined in 2D should be handled with care. Image analysis of thin sections with an ordinary microscope or a highly developed scanning electron microscope (SEM) adequately describes the pores in 2D, but necessitates stereology to calculate their position in 3D [21,22]. The typically used methods, like MIP, water vapor adsorption and nitrogen adsorption, are based on the assumption that the geometry of the pores is regular and that they are interconnected [16]. However, in natural building stone most of the time the pores are very irregular of shape (Fig. 1).

For information about the distribution sizes of pores in the specimen, obtained from mercury intrusion data, an appropriate model needs to be invoked [14,16,23]. The usual model is that of a system of cylindrical pores, each of which is entirely and equally accessible to the outer surface of the specimen. For porous systems, the well-known Washburn equation is often applied to estimate the

![Fig. 1. Pseudo-3D image of pore structure in sandstone (created with µCT/µCTanalySIS).](image-url)
diameter of the cylindrical pores, intruded at each pressing step:

\[ d = -4g\cos\theta/P \]

where \( d \) is the diameter of the cylinder being intruded, \( g \) is the surface tension of mercury, \( \theta \) is the contact angle of mercury on the solid and \( P \) is the applied pressure. With this model, there is no distinction between intrusion into a single long, continuous cylinder and intrusion into a multitude of shorter cylinders of the same diameter, as long as they are all open to the outer surface [14]. Due to the “ink-bottle-effect” MIP over-estimates the smallest pores and underestimates the bigger ones [14,16]. Although the MIP technique is widely used, it does not measure the true distribution of the pore size due to this ink-bottle-effect [16]. Because there is a need to have pore size distribution data in 3D, \( \mu \)CT turned out to offer a good alternative. When analyzing and describing pore structures in 2D, even in a very detailed manner based on SEM images, the 2D–3D transformation will always remain necessary. 3D analysis has recently been introduced in the study of pore structures. Warner [24], Hanson et al. [25], Peyton [26], Heijs et al [27], Perret et al. [28], Daniel et al. [29] and Pierret [30] used 3D visualization for the study of macropores. After the visualization of macropore structures, 3D quantification was soon introduced using computed tomography [30–34]. With the introduction of X-ray micro-tomography, pores with diameters up to 10 \( \mu \)m could be visualized and quantified.

The main topic in the present experiment will be to follow how porosity and pore size distribution changes due to treatment of water repellents and consolidants, and to determine the impregnation depth and localization of these products inside the stone samples with \( \mu \)CT.

2. Materials and experimental procedures

2.1. Stones

Two local natural building stones were selected for this study because of their high porosity and their pure (mono-) mineralogical composition.

(1) A quartz arenite of Upper-Landenian age (Lower Eocene) known as the Sandstone of Bray. This was used for the construction of important monuments in Binche, Mons and Bray (Belgium) [35]. This sedimentary detrital sandstone is a continental deposit mainly consisting of quartz grains consolidated with siliceous cement into concretions of irregular form [36].

(2) A highly porous bioclastic limestone from Maastricht (Maastrichtian, Upper Cretaceous). This yellow building stone can be found in Southern Limburg (Belgium) and in the region of Maastricht (the Netherlands) and is a typical building stone for the Romanesque and Gothic monuments of the Limburg province [37]. Very characteristic for this soft and porous stone, which offers good resistance to weathering, is the formation of a “calcin” which effectively protects the limestone against weathering [37]. This calcin is a thin superficial grayish layer of recrystallized calcite. It is created due to the action of rainwater, which dissolves the calcite crystals of the cement. When the raining stops, water starts to evaporate, transporting the calcite to the exterior face of the stone, where it recrystallizes. To develop a “calcin”, which can have a thickness of 1.5 cm, a succession of dry and wet periods is necessary.

2.2. Water repellents and consolidants

At present, more than 90% of the water repellents consist of siloxane [6] and they have performed well in several tests [5]. In this study, a methylethoxypolysiloxane was used as water repellent. For the consolidants, a product based on tetraethylsilicate was chosen. Ethylsilicates were used because literature studies suggested that best results in consolidation were obtained with this kind of consolidant [38–40].

2.3. \( \mu \)CT and porosity measurements

For our measurements, a “Skyscan 1072” microtomograph was used. Samples were scanned at a voltage of 130 kV and current at 76 \( \mu \)A. A random movement of 10 with a 4-frame averaging was chosen to minimize noise. The \( X, Y \) spatial resolution was 10 \( \mu \)m with the same resolution on the \( Z \) axis. Cores of 8 mm diameter were drilled from the stone samples.
Optimal parameters were used to reduce noise and artifacts (beam hardening, ring, star and line artifacts) inside the images during acquisition [41,42]. After acquisition, the images were further corrected by special tools in the reconstruction software designed to reduce beam hardening and ring artifacts.

To obtain 3D information from the created 2D images, new 3D software had to be developed (μCTanalySIS) [41,42]. This 3D software, which is also applicable on 2D images [43], first segments the image to select the objects of interest (in our case, the pores inside the stone samples). All the different objects (pores) are labeled, after which quantitative 3D interpretation, such as maximum opening, orientation and pore volumes, was performed [42]. Due to this 3D software, it is possible to obtain 3D data of the samples scanned with μCT. Because μCT is a non-destructive technique on small samples, those samples can be monitored during treatments with consolidants and water repellents. This allows quantifying changes inside the samples during these treatments.

3. Results and discussion

3.1. Microscopical description

The Bray sandstone shows more ‘sandy’ varieties, less cemented and with a higher porosity and more ‘quartzitic’ varieties, highly cemented and with lower porosity. The color of the stone varies over gray to yellowish brown, depending on the amount of iron oxide, which occurs as a very thin coating around the grains (Fig. 2). In addition to monocrystalline quartz grains and sometimes polycrystalline quartz, feldspars, rutile, zircon, some mica and clays can be identified. Some quartz grains show a typical overgrowth where, in many cases, the shape of the original grain is delineated by a thin iron oxide or clay coating between the overgrowth and the grain. The precipitation of the clay minerals in the sandstone is very significant as it can have a great effect on its permeability and porosity, and this may seriously reduce its reservoir potential. An average grain size situated between 0.125 and 0.25 mm was determined by means of point counting on thin sections. Grains range in size between 0.015 and 0.50 mm with a mean grain size (i.e. the average value taking into account the grain sizes at the 16th, 50th and 84th percentiles (Table 1) equaling 2.68Φ or 0.156 mm diameter (Fig. 3). Based on the grain-size scale for sedimentary rocks after Udden [44] and Wentworth [45], and Blair and McPherson [46], this value corresponds with the values for fine sandstones. Most of the grains are angular to sub-rounded, with a low sphericity. According to the formulae of Folk and Ward [47] (Table 1), the grains could be defined as poorly sorted and positively fine-skewed. For the kurtosis, which is based on the size of a distribution’s tails, the results gave an indication for a leptokurtic curve. In general, it seems there is no real preferred orientation of the grains and they are close packed with more concavo-convex contacts.

The Maastricht limestone consists mainly of skeletal components from foraminifera, sponges, bivalves, bryozoa and brachiopods, with calcite cement (Fig. 4). Chemically, this limestone contains more than 90% CaCO₃, together with small amount of SiO₂, Al₂O₃, Fe₂O₃, CaO, P₂O₃ and MgCO₃. By means of point counting on thin sections, the average grain size was determined to be between 0.125 and 0.25 mm (Fig. 5). The mean grain size of 2.22Φ, which corresponds with a fine sand grain size, is responsible for the sandy character this limestone has. According to the formulae of Folk and Ward [47] (Table 1), the grains could be defined as moderately sorted and fine-skewed.

3.2. Porosity

The total porosity of the sandstone and limestone samples was determined by means of water absorption under vacuum, MIP, 2D-image analysis of thin
sections and 3D-image analysis of μCT-derived images [42]. The average open porosity of the sandstone, determined with water absorption under vacuum was 14%, with a minimum of 4% and a maximum of 24%. The average open porosity of the limestone was 52% (±2%). The pore size distribution was determined with MIP and 3D-image analysis of μCT-derived images. For the sandstone, the average pore diameter determined with MIP ranged from 4.7 to 20.1 μm, with an average of 15.7 μm. The μCTanalySIS determined an average pore diameter of 26.6 μm for the sandstone. The difference between those two values has to do with the resolution of the μCT images and the fact that the digital images are divided into pixels. One of the most important limiting factors with the μCT is the intrinsic spatial resolution, which limits the smallest pore width that can be detected by μCT. Because in our case 1 pixel equaled 8.8778 μm, the smallest volume detected with the software was (8.8778 μm)³. The second object detected by our software was a volume with a diameter of three pixels, which is 26.6 μm. Because of these limitations, our software cannot distinguish pore sizes between 8.8778 and 26.6 μm diameter. With MIP, the average pore size of the limestone was 39.01 μm. The average pore size diameter determined out of the μCT images was 28.4 μm. In this case, the pixel size was 9.45 μm. The pore size diameter of the volume immediately larger than 28.4 μm (three pixels) was 47.25 μm (five pixels) diameter.

Table 1

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Graphic formula</th>
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<tbody>
<tr>
<td>Mean M</td>
<td>(Φ₁₆ + Φ₅₀ + Φ₈₄)/3</td>
</tr>
<tr>
<td>Median Md</td>
<td>Φ₅₀</td>
</tr>
<tr>
<td>Sorting σΦ</td>
<td>((Φ₈₄ - Φ₁₆)³ + ((Φ₀₅ - Φ₃))/6.6)</td>
</tr>
<tr>
<td>Skewness Sk</td>
<td>((Φ₁₆ + Φ₈₄ - 2Φ₅₀)/2(Φ₈₄ - Φ₁₆)) + ((Φ₂₅ + Φ₀₅ - 2Φ₅₀)/2(Φ₀₅ - Φ₃))</td>
</tr>
<tr>
<td>Kurtosis Kg</td>
<td>(Φ₉₅ - Φ₅)/2.44(Φ₇₅ - Φ₂₅)</td>
</tr>
</tbody>
</table>

Fig. 3. SEM image of Bray sandstone.

Fig. 4. Maastricht limestone.

Fig. 5. SEM image of Maastricht limestone.
It also has to be taken into count that MIP and μCTAnalySIS generate different results for the pore size distribution because both techniques are based on completely different physical principles [42]. The main limitation of the μCT is its resolution, which will be enhanced in the future.

3.3. Visualization of water repellents

Because water repellents tend to have a similar attenuation for X-rays as some of the minerals inside the scanned stone samples, no clear distinction between product and stone was visible in the first tests. This necessitated doping the water repellent with a 3-bromopropyltrimethoxysilane containing a higher attenuation for X-rays and could mix with the water repellent without chromatic separation inside the stone. By doping the water repellents, it became very easy to visualize them inside the stone samples. Fig. 6 illustrates a cross-section image derived from the μCT data of a sandstone sample, while Fig. 7 shows a similar stone where a doped methylethoxypolysiloxane was used. On the images, it is clearly visible that the product filled certain pores. To check if the doped product had the same water-repellent effect as the non-doped one, their capability was tested with the Karsten pipe method [6]. The Karsten pipe results showed no difference in water repellence between stones treated with a methylethoxypolysiloxane and doped methylethoxypolysiloxane.

A small cylindrical sandstone sample originally taken from a bigger sample was used for this research. The original stone had a total porosity of 13.6% and an apparent density of 2295 kg/m³, determined with water absorption under vacuum. The small cylinder was first impregnated with a 33% doped hydrofuge and then scanned with μCT (Fig. 8). Based on these images, the partial porosity inside the sample was calculated (Fig. 9). The water repellent was applied on top of the sample, but in the cross-sections in Fig. 8 it is clear that the water repellent impregnated the sample almost completely. The highest concentration of water repellent is visible in the cross-sections 16–25, but the water repellent is detectable throughout the whole sample. It is obvious that the doped methylethoxypolysiloxane did not concentrate only in the upper part of the sample. The same conclusion could be taken after analyzing the partial porosity results. The partial porosity results indicated that, due to filling of the pores, the average porosity was much lower. The partial porosity is extremely strongly influenced in the upper 2 mm. Because in most literature it is said that water repellent does not block the pores, this was examined with fluorescent microscopic investigation. The treated sample was, after scanning with μCT, impregnated with a fluorescent resin to fill the remaining pores. In total, six thin sections were made, parallel with the orientation of the cross-sections made with μCT: two times a thin section from the bottom area, two times from the
middle area and two times from the top area. One thin section was always covered with glass, for normal petrographical research, while the other one stayed uncovered for fluorescent microscopical investigation. The partial porosity results indicate a heterogeneous porosity inside the sample, which is partially due to the fact that different amounts of iron oxide around the grains spread over the entire sample (Figs. 10 and 11). On the μCT images and the results of the partial porosity, a higher porosity is detected in the superficial layer, where the water repellent was applied. The partial porosity results indicate that in the upper layer, which is 1 mm thick, the porosity is lower than 1%. To check this result, the thin sections were examined with fluorescent microscopy (Fig. 12). This shows that indeed a lot of pores were completely filled with the water repellent because no fluorescent resin, applied under vacuum, could enter certain pores.

The same procedure was followed for the treatment of a limestone. Here, the results turned out to be completely different. There was no filling of the pores at all and even with doping the water repellent, it could not be clearly visualized on the μCT images. This is probably due to the fact that the water repellent was spread all over the high porous sample, creating a thin film around the grains.

Although the same product was used for both stones, it reacted completely differently inside the stone because of the porosity differences between the rock types.

### 3.4. Visualization of consolidants

Consolidants have, like water repellents, a similar attenuation for X-rays as some of the minerals inside the scanned stone samples. To exactly visualize them, doping is needed. Because the consolidants have the capability to change the porosity inside the sample, this characteristic can be used to determine their impregnation depth. When a stone sample is scanned before and after treatment, the partial porosity indicates the penetration depth of the consolidant [42]. For this study, Maastricht limestone samples were treated with a tetraethylsilicate mixed with 3-bromopropyltrimethoxysilane in a 1/4 ratio. Visually no clear changes between the μCT images before and after treatment could be detected [42]. The 3D software however detected a decrease of the total porosity with more than 6% due to consolidation. The partial porosity suggested that the consolidant had an influence on the porosity of the whole sample, which was not higher than 2 cm. This was confirmed by the
SEM research and in the literature [6,38], where ethylsilicate was shown to have a large impregnation depth and tended to spread more equally over the sample instead of concentrating at the top. In the region where the consolidant was applied, porosity values were more reduced than in other areas of the sample. SEM images were taken in the top, the middle and the bottom part of the consolidated samples. The consolidant was visually detectable over the whole sample, with a higher concentration on the top (Fig. 13). The electron dispersive spectroscopy spectra also indicated the presence of the consolidant over the whole sample by detecting (besides CaCO₃ and traces of Si) the presence of Br used for the doping of the

Fig. 10. Thin section of an area with low amounts of iron oxide in the Bray sandstone.

Fig. 11. Thin section of an area with high amounts of iron oxide in the Bray sandstone.

Fig. 12. Images of thin sections from treated Bray sandstone. The left column is taken under fluorescent light, while the right column represents the same area taken under normal light. (a) Thin section in the upper part; (b) thin section taken in the lower part.
tetraethylsilicate. These results indicate that the consolidant did not just concentrate on the upper part of the sample, which could be harmful during further weathering.

4. Conclusions

X-ray μCT turns out to be a powerful tool in the research of water repellents and consolidants inside natural building stones. Based on the results of the visualization of the water repellent, it seems that the hydrofuge sometimes completely blocks the pores, although in theory most of the time it is thought to produce a thin film around the grains. The combination of these latest results together with the ones from the water repellent applied on the limestone of Maastricht shows that pores can be blocked by the water repellent depending on the total porosity and the pore size distribution. Further experiments will be performed to determine water vapor transport changes due to this treatment on stone with different porosity. The purpose will be to control if there is a link between the use of water repellents and porosity data of the stone material on one side and water vapor transport changes on the other.

A limitation of the μCT is that actually the smallest detectable pore will be 10 μm. Additional to the μCT technique, light optical microscopy and scanning electron microscopy research need to be performed, to see what happens in the total pore range. Already nano-CT is being introduced in research, indicating that this technique is making more and more progress with time and allowing more precise and detailed data.

This study opens the possibility for a whole range of studies. Topics like porosity changes inside stone samples during weathering can be investigated, as well as the way products react inside different stone types and how they react on certain weathering types.

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References


