X-RAY MICROTOMOGRAPHY-BASED LABORATORY STUDY
OF SULPHATE-INDUCED DECAY ON A GEOLOGICAL MATERIAL USED AS MONUMENT STONE

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ABSTRACT

This preliminary qualitative laboratory study aims to obtain, for the first time in our country, representative digital information on 3D spatial structure evolution of a cultural heritage geological material type, using a High Resolution X-Ray Computed Micro-Tomography, a 3D X-ray microscopy non-destructive technique. It is a study of a Portuguese travertine sulphate-induced decay process and it is an essential complementary step of a multidisciplinary project to be set-up in order to obtain in the future a valid methodology to better describe, model, simulate, forecast and understand that kind of environment-induced travertine degradation processes and phenomena. Therefore, this stone type is also simultaneously being studied by the combined application of more classical methods: Optical Microscopy, Scanning Electron Microscopy and Mercury Injection Porosimetry. These partial laboratory studies will be integrated in that methodology and also in future studies of other cultural heritage materials.

This study demonstrates the HRXµ-CT potential as a valid complementary tool, at least, to better study sulphate induced decay of complex natural materials in different environmental conditions, clearly enabling, at least in principle, suggestive valid qualitative estimation of environment/pore network texture (morphological/topological) evolution correlations at different spatial scales. Their quantitative assessment and statistical validation will be the next step.

INTRODUCTION

In the fields of Materials Sciences and Geosciences, it is well known that geologic materials used in cultural heritage decay as a result of the nature and dynamics of stone/environment interactions. These interactions are in general more or less complex phenomena, often combining inextricably mechanical, chemical, physical and biological processes. The ability of these factors to influence the nature of decay process in the wild, depends on the intrinsic properties of the material itself (which can be considered a random heterogeneous, multicomponent, multiphase, multiscale, more or less interconnected cracked and porous medium) and on the extrinsic characteristics of the environment the material is in contact with, which behaves more or less stochastically and can have a very high chemical and/or physical/mechanical potential to damage those materials. Depending on largely unpredictable changes in the nature and behaviour of the environment contacting the stone, fluid solutions may percolate through the spectrum of the stone voids network, eventually chemically reacting with the stone matrix and modifying the overall system
(voids (cracks + pores) network and matrix texture (morphology/topology/scale spectra), chemical/mineralogical composition and the percolating solutions as well). This way, ions may remain in solution or salts may precipitate and accumulate as water evaporates. It can be expected, at least, that such conditions are likely to induce more or less complex oscillatory chemical/physical/mechanical stresses contributing to the more or less complex behaviour of the decay processes. They can lead to distinct decay patterns not completely understood as yet [1-10], hindering rational design for long-term durability and affecting safety as well as economics/environmental sustainability of cultural heritage objects.

In particular, it is well known that sulphate ions present in soil, groundwater, seawater, decaying organic matter, acid rain and industrial effluent adversely affect the long-term durability of heritage materials worldwide. While, generally, soluble salts do not affect the structural stability of stone elements, erosion related to salt crystallisation could affect the aesthetic performance of natural stone that is presently mostly used as decorative material. The effects of soluble salts depend on environmental conditions, characteristics of solutions and properties of the affected materials (several examples can be seen [11-15].

Synthesizing, it can be considered that the scientific study of random heterogeneous materials damage depend heavily on the evolution of multiscale geometrical structure (texture) details, on the surface and on the interior of the material, induced by the influence of environmental factors. In particular the electrolytic solutions percolating the voids network system. Classical macroscopy and microscopy studies depend on the quality of 2D macroscopic and microscopic imaging techniques. So, it is natural to expect 3D qualitative and/or quantitative microscopy is becoming of utmost importance in characterizing internal structures of various complex materials types interacting with the above described environmental contexts. High Resolution X-Ray Computed Micro-Tomography (HRX\(\mu\)-CT) enables, in principle, new qualitative and/or quantitative approaches in petrological research of rock system components, such as the textures (morphology, topology and scale spectra) of the voids (pore+ fissure) and of the mineral matrix networks. Since traditional 2D imaging techniques do not produce the 3D resolution and material texture details HRX\(\mu\)-CT provide, it is important to combine its non destructive and 3D imaging characteristics with those of other 3D destructive and nondestructive methods like mercury porosimetry (MICP) and gas permeameters, respectively. This, in order to achieve better qualitative and quantitative integrated models, assessing their pore and matrix textures evolution and decay potential in different environmental conditions.

**EXPERIMENTAL & METHODS**

In this paper, a preliminary complementary X-ray Computed Tomography study describing results of sulphate salt degradation of a Portuguese cultural heritage stone type (Travertine) is presented, based on the Portuguese Standard NP EN 12370 (2001) to study the influence of salt-induced decay on petrological characteristics of the stone. A Portuguese geologic material type used as cultural heritage material has been selected because of its relatively high porosity and its almost pure (mono-) mineralogical composition: Travertine (T).

According to DGGM [16] the travertine from Condeixa-a-Velha (near the city of Coimbra, Portugal) is a tufa limestone formed by calcification of vegetal stalks and limbs. This same publication refers that a Plistocenic age has been attributed to these formations and also highlights its heterogeneous character. Regarding mineralogical data for these stone types [16, 17] for the travertine is indicated the presence of 1 % clay minerals and 99 % calcite [11] (figure.1).
This preliminary qualitative study of sulfate salt degradation of the stone is presented, based on the Portuguese Standard NP EN 12370 (2001) [18]. It started with the preparation of two sets of representative stone samples that were simultaneously studied. One was classically studied by optical microscopy (petrographic characterization), scanning electron microscopy (SEM, analyses performed at CEMUP, University of Porto) and by X-ray diffraction. Details in [19]. The other was used as the samples feeding this preliminary HRX\(\mu\)-CT step. The travertine samples (T)-15.5x15.5x19.5 mm\(^3\)) were scanned with a compact desktop high resolution Skyscan 1172 microtomograph. This limestone type was also simultaneously being studied by the combined application of more classical methods: Optical Microscopy, Scanning Electron Microscopy and Mercury Injection Porosimetry (MICP) to be integrated in future quantitative studies of other dimension stones.

Considering it is rational to think that advantages are obtained if individual representative samples can be examined non-destructively several times during the course of natural or artificially-induced environmental interactions and that HRX\(\mu\)-CT can image the internal structure/texture of visible light optically opaque samples with spatial resolution in the range to that of optical microscopy, this study applies a method that has been developed and adapted for employing microfocal-based HRX\(\mu\)-CT systems for static texture scanning characterization. It was designed to be usable on typical systems [20, 22-25]. In principle, a series of views through the sample (i.e., radiographs taken along different directions) are recombinied mathematically into a cross-sectional map of the specimen's x-ray absorptivity; microtomography instrumentation and earlier work are reviewed elsewhere [20-24]. In particular, the HRX\(\mu\)-CT device consists of the combination of an X-ray radiography microscopic scanner system and a computer with tomographic acquisition, reconstruction and analysis software packages [21]. The Skyscan 1172 contains an X-ray micro-focus tube with high-voltage power supply, a specimen stage with precision manipulator, a 2-D X-ray CCD-camera connected to the frame-grabber and a Dual Pentium computer with colour monitor. In order to obtain high-resolution images, small samples are preferred. X-ray source and detector are fixed while the sample rotates around a stable vertical axis. The following procedure was used: The parallelepiped shaped samples were cut from the same stone macro samples used for the complementary classic methods integrated study referred above. Samples were scanned at a voltage of 100 kV with current intensity at 100 \(\mu\)A. A random movement of ten with a five frame averaging was chosen to minimise noise. The XX, YY spatial resolution was 6.76 \(\mu\)m with a 14 \(\mu\)m resolution on the ZZ axis. During information acquisition, X-ray radiographs were recorded at different angles during step-wise rotation between 0 and 180° around the vertical axis. The basic physical parameter quantified in each pixel of a CT-image is always the linear attenuation coefficient. To obtain 3-D information from the radiographic images produced by the X-ray microtomograph, reconstruction software package had to be used. The

![Figure 1: Travertine sample (15.5x15.5x19.5 mm\(^3\)) photographic images in two perspectives.](image-url)
images always contain a certain amount of noise that should be reduced. The X-ray microtomograph operation procedure was optimised to produce the best images by reducing artefacts like beam hardening, ring, star and line artefacts as much as possible [20, 22-25]. To reduce these artefacts, an Al-filter is placed between the X-ray source and the object to absorb the low photon energies. Line artefacts are bright lines due to abnormally bright pixels in the detector during one radiograph. Very dense inclusions can create a secondary radiation resulting in star artefacts, also reduced by the Al-filter. Ring artefacts appear as circles centred on the rotation axis and are caused by detector inaccuracies. To minimise ring artefacts, a random movement is applied on the object, together with its active area on the detector [20, 22-25]. After acquisition and correction, the image data can be qualitatively and/or quantitatively interpreted using 3-D analysis software [21]. This software enables quantification of petrographic/petrophysical rock properties such as maximum opening, orientation, pore volumes and quantification of necks when they are visible in the samples. The pore size distribution can be determined by the maximum opening, which is the biggest inscribed sphere of each pore. Erosion and dilation of the binary network with a spherical structural element determine this maximum opening.

RESULTS & DISCUSSION

For the studied sample the 3D spatial structure/texture information was reconstructed, in a model consisting of about 980 slices (8bit digital images) of the sample, using the CT-Reconstruct software package [21]. The slices (representing cross section elementary volumes of the sampling) can be integrated along the ZZ axis with a resolution of about 14 µm using the CT-ANT software package [21], reproducing a 3D image of the object (rendering process) or part of it. The virtual sample model can be manipulated in the 3D image space for better 3D microscopy (figure 2).

In figure 2 the three perspectives a), b), c) were obtained after the following steps: 1- Volume rendering corresponding to a virtual 3D model of the sample (considered here composed of matrix and voids); 2- Visual assessment of the linear correlation between the sound sample and its virtual model (this step enabled to consider the virtual model as very high quality one); 3- Virtual flat cut parallel to the top surface (orthogonal to the ZZ’ vertical axis) of the model, located about 3mm far from the top (obviously not visible in the shown perspectives) of the model; 3- Elimination of the lower part of the virtual object. The virtual lower surface clearly defines the spatial structure of the object local cross section 3mm far from the top surface; 3- Rotation of the retained part of the object enabling to see the a), b), c) perspectives.

The good quality of the 3D perspectives depicted in figure 1a), b) and c) results from the quality of the virtual model of the sample. They confirm locally the morphological, topological and multiscale complexity of the pore network system details in the interior and on the surface of the upper quarter of the sound travertine sample. This observation are reinforced observing figure 2 d), where, in a spectacular perspective of the model, some details can be seen of the complex multiscale spatial structure (morphology/topology) of the pore system network which are impossible to be non-destructively assessed using 3D destructive microscopy methods, not to mention 2D image ones.

Furthermore, considering the detailed evolution of the surface and of the interior of the sample (material and pores network), they can be clearly visualised and even locally quantified all along any of the 980 elementary volume slices composing the virtual sample (which is not presented in this paper). An example is presented in figure 3, where, in order to illustrate the evolution of the travertine interior, a representative reconstructed and binarised slice of the sample was selected, corresponding as far as possible to the same slice (the same elementary sample volume/slice) of the sample, from initial (step 0) and from even steps (steps 2,4,6,8,10,12) of the 15 steps cycle of the
Standard. Qualitative changes in the texture (morphology/topology, scale), within and on the surface of the slice along different steps of the samples can be clearly seen and assessed at least visually, comparing the binary images depicted in figure 3. The reconstructed image scales enable semi-quantitative estimations of those changes as well.

Detailed qualitative visualization of the evolution (even steps 2-12) of the sample as depicted in the reconstructed cross sections shown in figure 3 confirm that the spatial structure of the pore network details significantly change along the different steps of the decay process modifying the spectra of morphological, topological and multiscale details complexity of the macro and microscale pore network system towards a steady increase in the macro and micro porosity as well as the roughness of the surface of the pore system on the surface of the sample (this can be, for instance, quantified by a change in the fractal dimension of the pore/matrix interface surface). In the interior of the slice, there seems to be a more erratic curious behaviour, since there are some regions where porosity seems to increase compared to other regions where it seems to decrease. This suggests a globally complex dynamic dissolution/precipitation and mass transport process occurring inside the pore network system during the different steps of the laboratory study, towards a net decrease in the overall mass of the sample, corresponding to the sulphate-induced decay process.

Figure 2: - 3D Perspective views of the interior and the lateral surface of the upper quarter of travertine sample: a),b),c).
-3D perspective view of the pore system texture of the same sample: d).
Figure 3: Qualitative visualization of the spatial structure evolution (even steps 2-14) of the same horizontal slice of the model, corresponding to the lower quarter of the interior of the sample. Step 0 corresponds to the sound state of the travertine sample.
CONCLUSIONS
This study demonstrates the applicability potential of micro-tomography in providing new insights and guidance to prepare more systematic and detailed investigations on stone decay, enabling integrated research for more rational design and control of salt induced decay of these geological materials. This is not only because of the relatively easy 3-D information visualisation and quantification potential of HRXµ-CT, but also of its non-destructive character as well. Within the context of a broader implicit program aiming to set-up better qualitative and/or quantitative integrated multidisciplinary research and combining nondestructive 3D materials structural properties visualization and/or quantification, this preliminary methodological study, applied X-ray microtomography to study a cultural heritage materials, demonstrating the applicability potential of micro-tomography in providing new insights and guidance to prepare more systematic and detailed investigations on stone decay is possible in principle. This because of relatively easy 3-D information visualisation and quantification and non-destructive character, enabling integrated research in order to prepare better valid models to simulate and/or understand a kind of environmentally induced degradation phenomena for more rational design and control of salt induced decay of these geological materials.

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