

EVALUATION OF POROSITY IN MORTAR BY X-RAY MICROTOMOGRAPHY (MICRO-CT) AS AN ADDITIONAL TOOL FOR MERCURY INTRUSION POROSIMETRY

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Abstract: The evaluation of internal structures of cementitious materials represents a challenge for the engineering. The X-ray microtomography (micro-CT) is a technique that provides details of the object with a high resolving power (on the order of microns), allowing the visualization of the sample internal structure. This paper studies the evaluation of porosity of mortar by micro-CT and compares it with results obtained by mercury intrusion porosimetry, thus verifying the potential of each test in the identification of the size of pores. We evaluated the porosity of mortar with mixing proportions of 1:0:3, 1:1:6 and 1:2:9 (cement: lime: sand) by volume. The results allowed the characterization of the samples internal structures and the evaluation of mortars porosity. It was established that the micro-CT can be used as a complementary technique, because it identifies pores smaller than the ones identified by mercury intrusion porosimetry.

Keyword: Mercury porosimetry; Pore Size Distribution; X-ray Micro –CT; Mortar.

1. Introduction

Mortars are porous materials with a heterogeneous and complex structure, making difficult their characterization. The pores and voids of a material can be represented by different amounts, sizes, shapes and distributions. It is hard to evaluate this internal structure and represents a challenge for the engineering. Currently, the technological development of cement based materials is intimately connected to the study of the microstructure and porosity of those materials (DULLIEN, 1979; MEHTA, MONTEIRO, 2008).

The porosity affects the durability of mortars because it is a parameter linked with the action of potentially aggressive agents (air, water, gases and vapors) and it is particularly important to trap moisture and to encourage mold growth. Data on the total porosity of a mortar and the distribution of pores in its microstructure allows inferences about the phenomena that affect its performance as well as to complement the analysis of the mechanical characteristics of those materials (QUARCIONI et al., 2001).

The identification of the porous structure of mortars in solid state is limited. Currently, there are techniques of fluid intrusion in the pores of specimens aiming to verify the amount and distribution of pores size, but this verification is obtained indirectly through a correlation with the pressure with which the fluid is introduced into the specimen. This essay also presents difficulties in characterizing large pores. Large pores can be reached only through small pores; they will be registered as small pores, which results in a distortion of the results (DIAMOND, 2000; WILDS, 2001;

CHATTERJI, 2001). Figure 1 illustrates the interference of the porous structure on the properties of cementitious materials depending on the size of the pores.

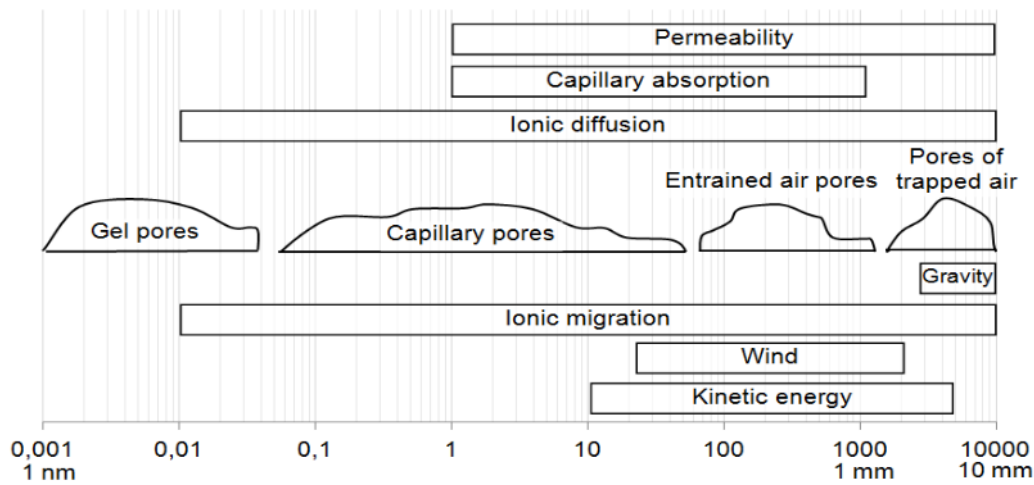


Figure 1 - Influence of pore size on the properties of cementitious material (HELENE, 1993)

Figure 1 shows that there are several sizes of pores that interfere with the properties of the cementitious materials. These sizes are hardly identified by just one test method, because the accuracy of each one is limited to a range of sizes. The observation of the porosity becomes complicated due to the physical structure of the complex of cement-based materials. These materials are heterogeneous at multiple scales and difficult to characterize, as shown in Figure 2.

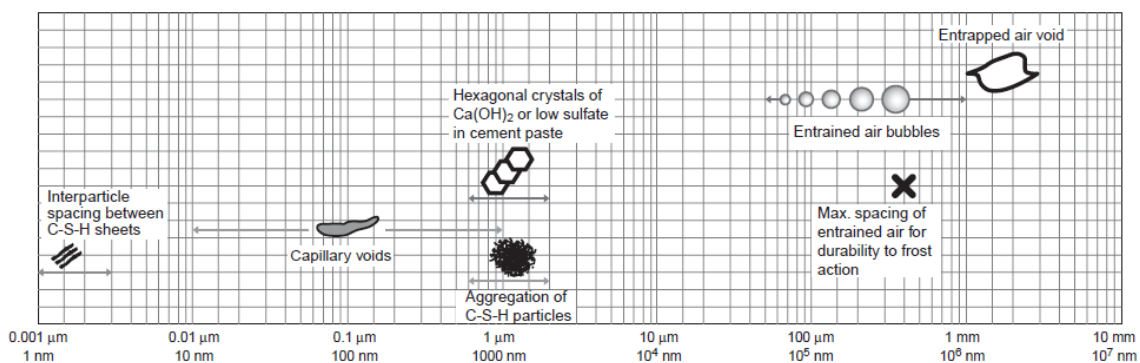


Figure 2 - Dimensions of solids and pores in hardened cement paste (HELENE, 1993)

A technique that would allow the visualization on a common scale (representative specimen) up to a wide range of magnifications would be useful. Figure 2 shows that several different pore sizes are possible to be found in cementitious materials. It is probably not possible to visualize all the pore sizes with just one technique. With the development of computerized systems, digital processing of images obtained by microscopy (optical or electronic) has been applied. Thus, the quantification of features such as porosity, pore size and shape is possible. Figure 3 shows the pore size range that some methods of porosity characterization can reach in order to identify the porosity.

Characterization method	Measurement limits (μm)							
	0,0001	0,001	0,01	0,1	1	10	100	1000
Optical microscopy						←	→	
Electron microscopy				←	→			
Mercury intrusion			←	→				
Nitrogen adsorption		←	→					

Figure 3 - Measurement capability of the various methods of characterization (FITZNER, 1994).

The several methods referred essentially allow the determination of the size and/or of the pores specific surface of the. As Sing (2004) refers, the methods to characterize porous materials should evolve up to the possibility of evaluating properties such as the exact shape of pores and surface roughness.

Mortars are generally optically opaque, however, many times characterizing the inner part of the sample without damaging it is desired because it prevents changes in the surface near the physical or chemical structure, which may occur during the sample preparation (e.g., cutting, polishing, fitting to the form) or environmental exposure (e.g., carbonation, leaching). In some cases, the surface may not be representative of the characteristics (LIMA, 2007). Thus, techniques such as x-rays that warrant the sub-surface and/or volumetric characterization are likely to be useful.

Computerized tomography (TC) is a non-destructive technique that provides information about the positioning and three-dimensional (3D) detail of a scanned object and, among others, the internal structure of the same (BALL, PRICE, 1995). The X-ray computed microtomography (Micro-CT) has the same foundations of the computerized tomography and is an advancement over X-ray inspections because it is a non-invasive procedure with a high resolving power (of the order of microns).

Promentilla et al. (2008) studied the porosity of cementitious materials and Promentilla, Sugiyama (2010) studied the porosity and cracking of mortars with micro-CT, getting satisfactory results but using just this method on the analysis. Naik et al. (2005) also evaluated cementitious materials, specifically with regard to sulfate attack, and noted the importance of using two methods (micro-CT and energy dispersive X-ray diffraction - EDXRD) to get more reliable results.

Therefore it seems appropriate that the development of mortars research also considers a different approach from the usual, due to the large range of pore sizes to be identified. The conventional essays, such as porosity by Mercury intrusion and theoretical methods, are important for a distinct range of pores, but there is a need for alternatives that complement the characterization of lower size ranges, due to the variability of this material.

The aim of this paper is to evaluate the porosity by micro X-ray computed tomography (micro-CT) of mortars and to compare the results with the ones of mercury porosimetry. The goal is also to verify the feasibility of the technique of micro X-ray microtomography as a complement to the techniques currently applied.

2. Experimental procedure

The specimens of mortar used were CP-II-F-32 cement (NBR 11578, 1997), CH-III lime (NBR7175, 2003) and sand industrialized from crushing. Preliminary characterizations of the materials are shown in Table 1.

Table 1 - Characterization of materials for mortar

	Cement CP-II-F-32	CH-III lime	Sand industrialized from crushing
Apparent density (g/cm ³)	1.08	0.68	1.66
Specific gravity (g/cm ³)	3.11	2.24	2.76

The mortars were prepared according to NBR 13276 (2005). The amount of water was determined by the consistency index according to NBR 13276 (2005), a consistency of 250 mm \pm 10 mm was fixed for all samples. The mortars were molded in prismatic molds (4 x 4 x 16 cm) using a vibrating table.

In this study all measurements were made using a microtomography desktop system (SkyScan -1172; SkyScan, Belgium) (Figure 4), with a high voltage (100kV), a microfocus x-ray source, a specimen holder with a precision manipulator and, as a detector, a 10Mp (4000 x 2300pixel) CCD camera connected to a control and data acquisition computer host which was linked to networked computers in order to reconstruct tomographic images. The tests were performed at the Laboratory Analysis of Minerals and Rocks (LAMIR), at the Federal University of Parana - UFPR, Brazil.



Figure 4 - SkyScan 1172 high-resolution micro-CT

The technique of X-ray microtomography differential is related to the size of the X-ray tube focus. This parameter can change from 4-1 mm (normal focus) to 100 to 1mm (micro focus) passing through the dimensions of 1 to 0.1 mm (mini focus). The small diameter of the X-ray tube focus is an important attribute of micro-CT testing. This happens because the smaller this parameter is, the better targeting of inspected structures it will have, which is related to the image quality acquired on the test.

The acquisition of tomographic images (cross sections) is performed in two steps:

- a) acquisition of radiographic images from different angular projections of the sample along a rotation of 180° or 360° with very accurate rotational steps (a few tenths of degrees); this acquisition is represented in Figure 5;

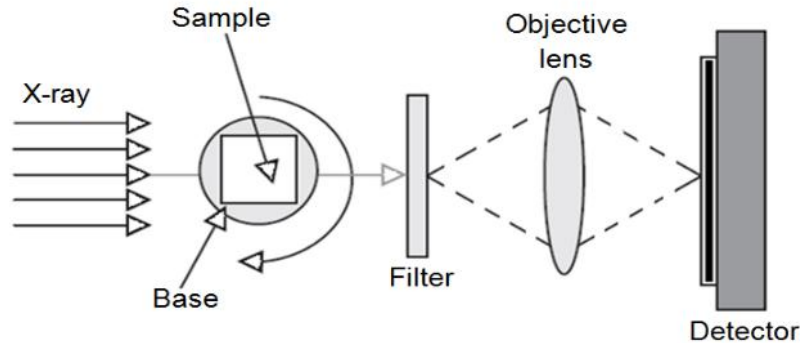


Figure 5 - Diagram of image acquisition by Micro-CT

- b) reconstruction of cross sections images from the ones of angled projections through the modified Feldkamp algorithm that is processed in the computers cluster. This rebuilding process creates a complete 3D representation of the internal microstructure of the object, as schematized in Figure 6.

The digitalization process is performed from a sample of the gray scale image (Figure 6b), which gives an idea of what may or may not be an empty space in the sample. It should be noted that this procedure depends strongly on the sensitivity and experience of the operator.

At the moment of digitalization, the sample is transformed into an image of two colors, or two phases, so it is the operator who selects the shade of gray to characterize what is a pore and what is mortar (Figure 6b). The Mercury intrusion porosimetry test was executed in collaboration with the laboratory of the Department of Materials Engineering, State University of Ponta Grossa, Brazil.

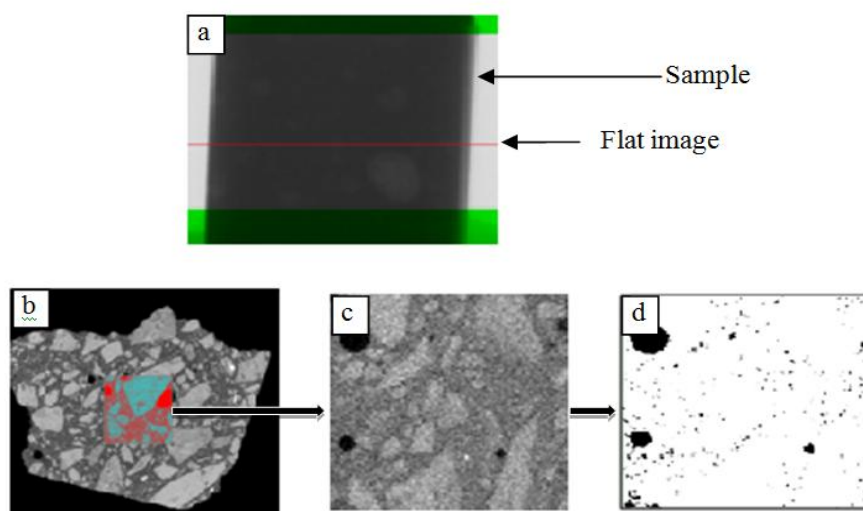


Figure 6 - Scanned images: (a) X-ray shadow of a typical sample of cementitious material, (b) cross section, (c) of the area selected for analysis, and (d) the processed data from the plane digitalized sample selected in order to only show the pores regions (black areas).

The mortar samples were tested following procedures recommended by the equipment manufacturer. The specimen is subjected to drying and degassing. After this step the specimen is placed in the capsule of a penetrometer; the test begins by a significant reduction in pressure, followed by the intrusion of the amount of mercury needed to fill the capsule and the penetrometer rod.

The penetrometer starts the process of gradually increasing pressure, which causes the intrusion of mercury in the porous structure of the specimen, usually by pre-defined levels. This process is split into two phases, the first one corresponding to a maximum pressure slightly above the atmospheric one and the second one to a maximum pressure given by the operator. After reaching the maximum value the pressure drops to atmospheric levels, in what is called extrusion. The software registers the series of values of pressure/volume levels of mercury introduced (or extruded).

Whereas the volume of mercury that penetrates the specimen corresponds to the accessible pore volume, the recorded data can be processed to obtain the set of pores volumes that have a given diameter.

3. Results and discussion

After defining the parameters of image display, which aimed to achieve the same shade of gray for digitalization and therefore a better differentiation between the images, it is possible to see in Figure 7 the differences between samples with different proportions of mortars: 1 : 3 (Figure 7a), 1:1:6 (Figure 7b) and 1:2:9 (Figure 7c).

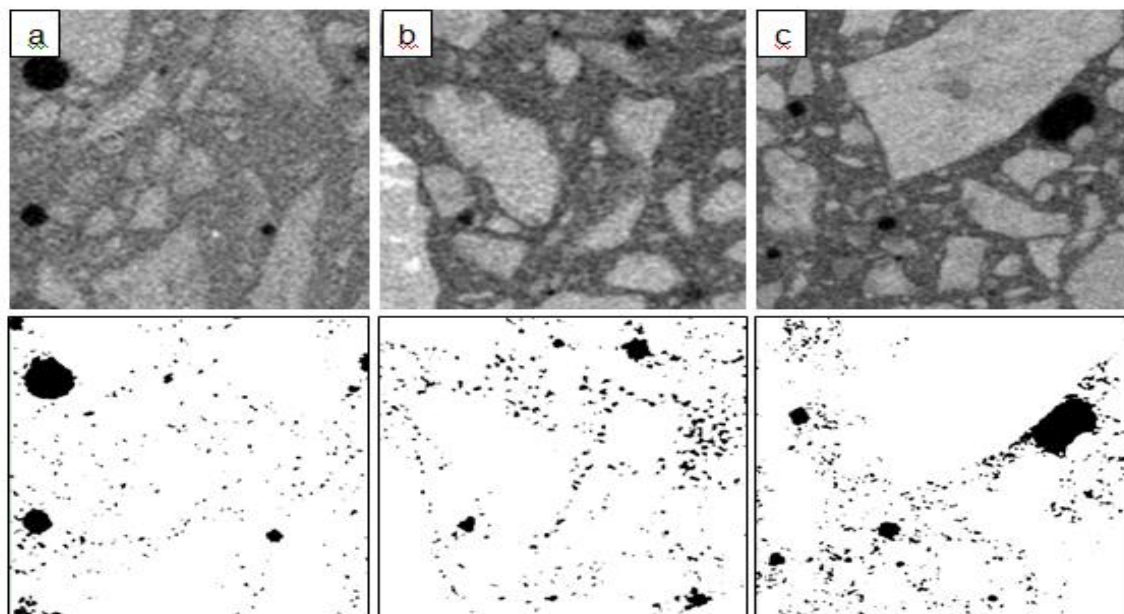


Figure 7 - Digitalization of mortar samples. Proportions of Mortars: (a) 1:3, (b) 1:1:6 and (c) 1:2:9

Although the same parameters were adopted for analyzing the images in microtomography, the samples did not show the same amounts of contrasts in the levels of gray tones. This effect happens because the digitalization depends much on the operator (the digitalization is very delicate/sensitive on mistakes by the user). Figure 7 shows the digitalization of images of mortar samples. It is possible to observe on the images that there are differences in the contrasts between the levels of gray, making it

difficult to define the level of gray adopted for digitalization. Table 2 shows the numerical results obtained from analysis of the samples.

Table 2 - Quantification of the porosity of mortars obtained by microtomography.

Description	Mortar			Unit
	1: 3	1: 1: 6	1: 2: 9	
	Value	Value	Value	
Total volume	142.2	127.1	127.9	mm ³
Solids	135.1	119.3	114.3	mm ³
Solids content	94.9	93.8	89.4	%
Number of closed pores	18929	19412	25514	
Volume of closed porosity	6.1	2.6	0.9	mm ³
Closed porosity content	4.3	2.1	0.8	%
Volume of connected pores	1.1	5.2	12.7	mm ³
Connected pores content	0.7	4.1	9.9	%
Volume of total porosity	7.1	7.8	13.6	mm ³
Total porosity content	5.0	6.2	10.6	%

The table shows that mortar 1:2:9 (with higher content of lime) is more porous (10.63%) than 1:1:6 (6.18%) and 1:3 (5.02%). It is possible to verify that the mortar with a higher level of lime, had a higher number of closed pores (25 514), plus an open porosity (9.9%) significantly different from the other mortars. This porosity may lead to an increased permeability of the sample in solid state which can be harmful due to transport of damaging agents. Figure 8 shows the curves of pore sizes distribution of mortar samples in logarithmic scale.

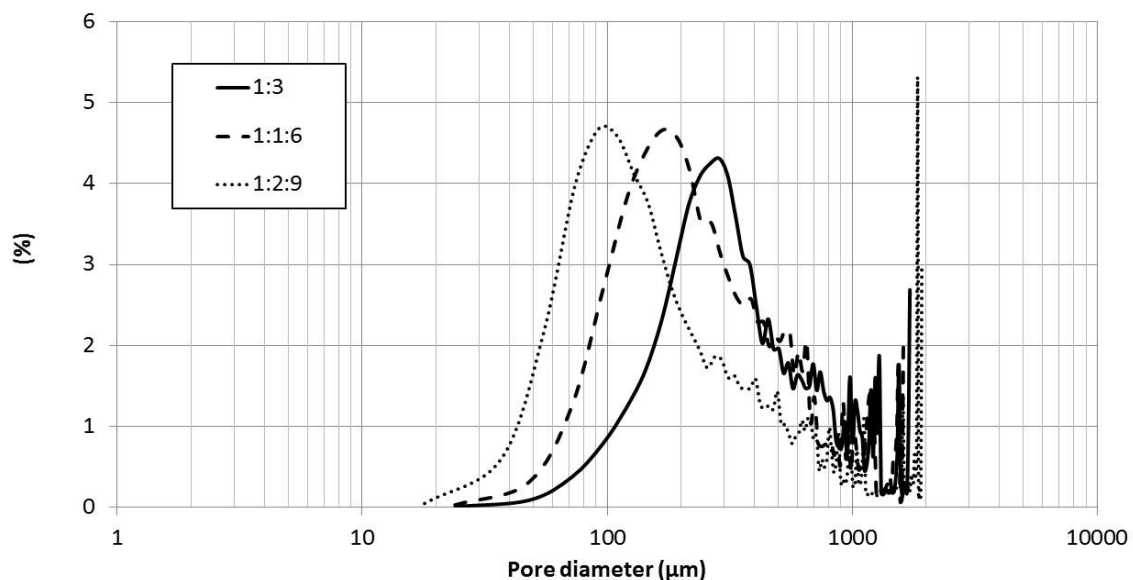


Figure 8 - Curves of pore size distribution in mortars by microtomography testing.

From the curves it is possible to visualize that the mortar 1:3 has a lower amount of small pores and higher porosity in larger pores. This may be due to the type of filler in the mixture, which contains only cement as a binder, while other mixtures have hydrated lime added to the cement. Probably the lime content is fomenting the formation of small pores. It is also possible to see a peak in pores with a diameter

smaller than 100 microns that can be checked in detail by the mercury intrusion porosimetry shown in Figure 9.

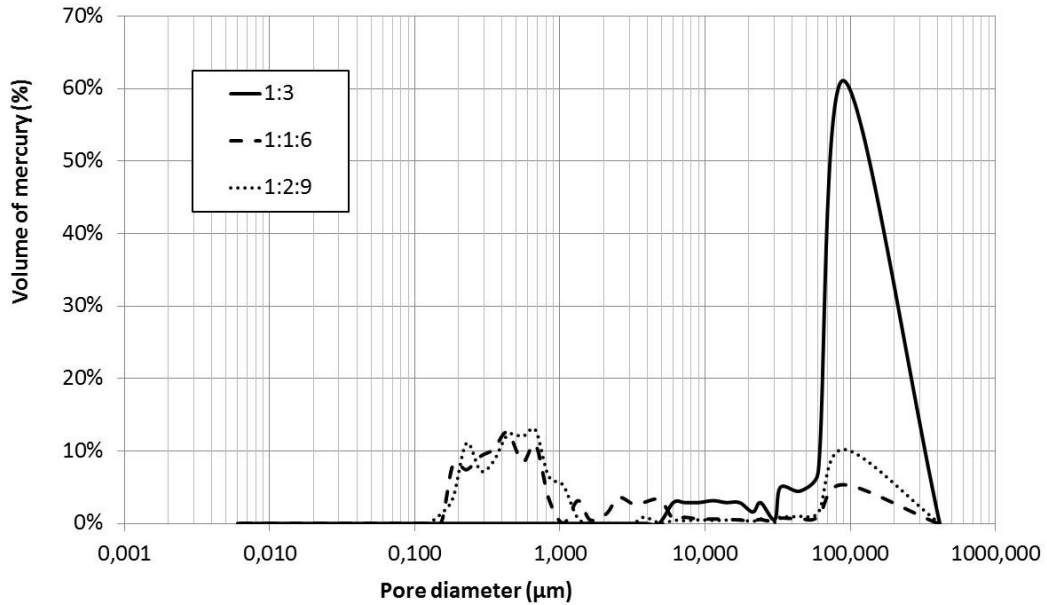


Figure 9 - Curves of pore size distribution of mortars by mercury intrusion porosimetry

It can be verified by mercury intrusion test that samples containing hydrated lime have a greater amount of smaller pores than cement mortars (1:3), as was also viewed in microtomography. This can be justified by the presence of lime in these mixtures, which have smaller grains than those of cement mortar in addition to generating a better workability to the mix and ensuring the best packing of particles, thus the pores can be made smaller. Figure 10 shows the results of mortars tested in mercury intrusion porosimetry and the results by microtomography.

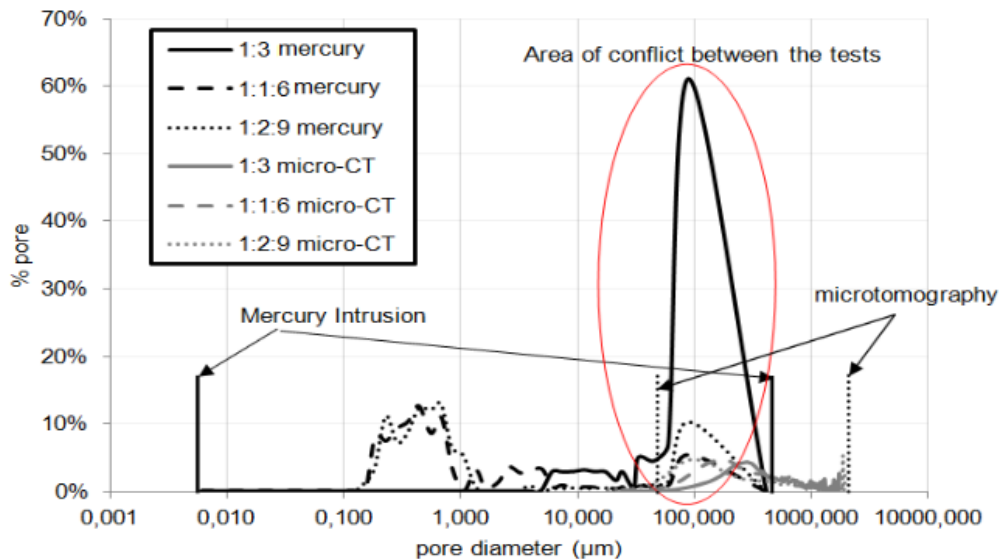


Figure 10 – Mortar size distribution by pore size using mercury intrusion porosimetry and microtomography

It is evident that the test for mercury intrusion is limited to the observation of a pore size of approximately $400\ \mu\text{m}$ ($0.4\ \text{mm}$). The microtomography can evaluate the porosity range up to $1800\ \mu\text{m}$ ($1.8\ \text{mm}$), but it has limitations in the observation of pore sizes smaller than $10\ \mu\text{m}$ ($0.01\ \text{mm}$). From these observations it was concluded that the tests may be complementary, thus contributing to the understanding and knowledge of the hardened cement structure porosity, since it is possible to achieve a larger and more complete range of pore diameters.

As observed in literature review, the test of mercury intrusion porosimetry neglects some large pores. For the mercury to reach those pores it has to pass through small pores. The test result of mercury intrusion porosimetry shows a small amount of pores that is not real, as can be verified by microtomography. The microtomography, because of the maximum resolution that can be achieved, compromises the viewing of small pores

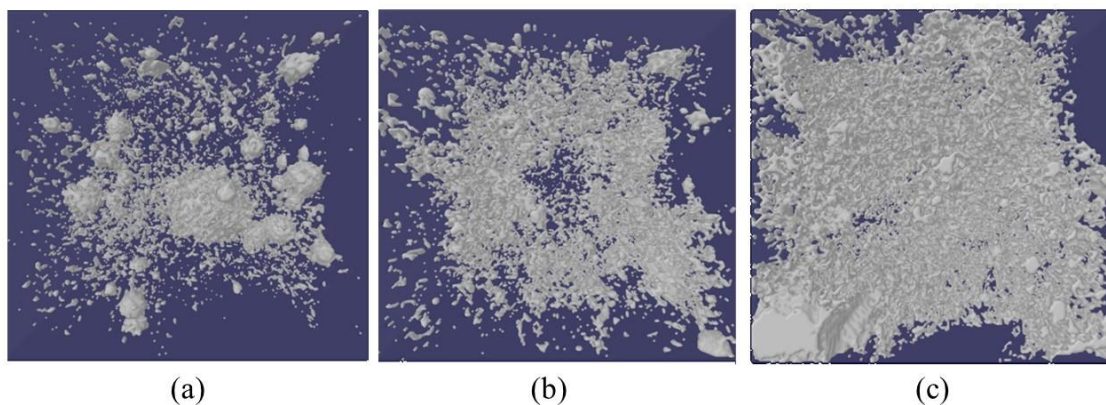


Figure 11 - Images of the porosity of mortar samples in 3D: (a) 1:3, (b) 1:1:6, (c) 1:2:9.

Another point observed was the conflict between the tests, because the cement mortar showed discrepancy in pores size in the range of $100\ \mu\text{m}$ micro-CT test, which was not confirmed by testing microtomography. After reading the results, the 2D images were rendered to show the 3D sample. Figure 11 shows those renderings. The images make clear the difference in mortars porosity. Mortar 1:2:9 has a significantly higher porosity than the others.

4. Conclusions

The results show that the evaluation methodology for porosity microtomography is important for the characterization of mortars; it allows the visualization of pores in the range of $10\ \mu\text{m}$ to $200\ \mu\text{m}$, making possible to obtain a distribution curve of pore sizes in that range.

In the mortars it was found that the one with higher concentration of lime has a higher porosity. The results also showed the difference in observations between the two test methods. The test for mercury intrusion porosimetry characterizes better the small pores, while microtomography scans the large pores. So the combination of those techniques will contribute to a greater knowledge and understanding of the porosity of hardened cement structures.

It is worth to mention the possibility of 3D visualization of the samples analyzed by micro-CT; therefore it is also possible to check details about the orientation and distribution of the pores.

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