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Penetration of the consolidant Paraloid® B-72 in *Macuxi* indigenous ceramic vessels investigated by neutron tomography

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ABSTRACT

The neutron tomography technique was applied in studying the penetration of the consolidant Paraloid® B-72 in contemporary indigenous ceramic vessels. The study was carried out for two distinct and controlled air humidity conditions, 40% and 90%, in which the vessels were exposed, before the consolidant application. The obtained images have proved that the penetration of Paraloid® B-72 in the ceramic does not depend on the humidity condition in which it was applied, moreover allowed a macro-visualization of the consolidant penetration in the ceramic vessel. As the vessels used in the present work were manufactured by an indigenous artisan, *Macuxi*, according to the same procedures and raw materials used by the ancient artisans, the results obtained can be used as a guide to assist experts, both in the study of archeological objects of *Macuxi* origin, as well as other objects that had been made by other tribes that lived in the same Amazon region, in Brazil.

1. Introduction

Objects manufactured out of clay are present in many cultures over several epochs of civilization. In Brazil, ceramic objects date back to 2000 BC, especially those produced on Marajó Island [1,2]. Before the European arrival in America, there were about 5 million natives living in the Brazilian territory. They were divided in tribes according to the linguistic affiliation in Tupi–Guarani (Coast), *Macro-jê* (Central plateau), *Aruak* and *Karib* (Amazon). Particularly, the *Macuxi* tribe speaks a language derived from the *Karib* family, and since the middle of the XVII century, they live in the northeast of the Roraima State, between the Branco and Rupununi river heads, on the border of Brazil and Guiana. Besides the *Macuxis*, other tribes like *Yanomami, Ingarikó, Wai-wai, Patamona, Wapixana, Waimiri-atroari, Yekuana, Taurepang, Arekuna and Kamarakoto*, lived in the same region, and because of the closeness, the tribes are social and culturally alike [3]. Their rich cultural heritage includes, among others, the manufacture of objects, and for the purposes of the present work, the ceramic ones will be emphasized.

In order to preserve archeological ceramic objects, it is usual the employment of restoration techniques to prevent deterioration caused by decomposition or fragmentation processes. In such cases, the restorers usually make use of specific organic substances known as consolidants, which are applied to the surfaces of the objects to be restored. These substances are acrylic polymers that, after application, penetrate by the pores of the ceramic forming a protective film on its surface. Both the penetration as well as the distribution of Paraloid® B-72 within the structure of the object of interest are key factors to the effectiveness of the employed restoration technique [4–8].

The objective of the present study was to investigate the penetration and the distribution of the consolidant Paraloid® B-72 in *Macuxi* contemporary indigenous ceramic vessels, by means of the neutron tomography technique. The consolidant was applied in two humidity conditions in which archeological objects are usually found in the Brazilian Amazon [9].

2. The ceramic samples and the consolidant

The ceramic samples studied in the present work were contemporary vessels manufactured by an artisan of the Brazilian tribe *Macuxi*, making use of the same manufacturing process and raw-materials used by their ancestors. The raw-material is clay which, after being collected close to the indigenous settlement, is dried in the environment and crushed using a wooden pestle. The crushed clay is slightly moistened and the vessels are hand molded and dried in an ordinary campfire [9]. The resulting vessels are not uniform both in shape as well as in thickness. Their maximal external diameters vary from 85 to 90 mm while the thickness of the walls, from 5 to 9 mm. Typical vessels are shown in Fig. 1.

The consolidant Paraloid® B-72 is an ethyl methacrylate (70%) and methyl acrylate (30%) copolymer which, for the purposes of the present work, usually is diluted in acetone P.A. 10% in mass [4–8].

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Fig. 1. Typical ceramic vessels studied in the present work.

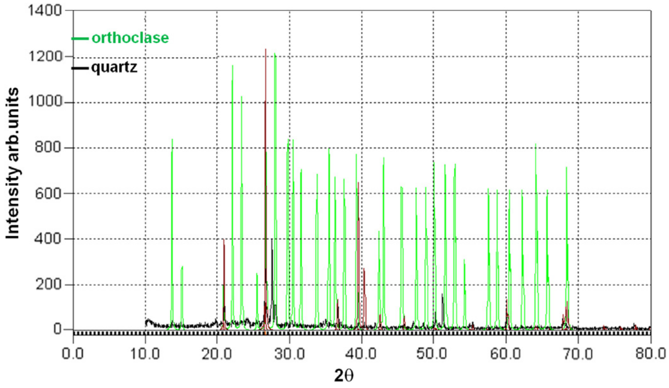

Fig. 2. X-ray diffractogram of the studied ceramic.

Two vessels were prepared for tomography. They were kept for seven days at atmospheric pressure, at two air relative humidity (RH) conditions, 40%, and 90%. After this period, the Paraloid® B-72 solution was applied in its outer walls using a brush [7]. They were kept in the laboratory (T = 24 °C, RH = 64%) for 3 h to dry the acetone, prior the irradiation takes place.

2.1. Ceramic characterization

2.1.1. Mineralogical composition

The composition was determined by X-ray diffraction (XRD) and for such purpose, one of the vessels was crushed (~30 μm grain size), in a porcelain mortar, and a small fraction of the powder was analyzed in a Rigaku (Multiflex) X-ray diffractometer. The result obtained in Fig. 2 shows that the ceramic mainly consists of Quartz (SiO_2) and Orthoclase ($KAlSi_3O_8$) [7,10].

2.1.2. Ceramic surface

The surface was studied by Scanning Electronic Microscopy (SEM). Two fragments of two vessels, the first without and the second with Paraloid® B-72, were imaged in the electronic microscope FEI (mod. QUANTA 400 FEG). The Fig. 3(a) is the image of the first fragment showing some pores and cracks with irregular contours. The Fig. 3(b) shows the second fragment in which the Paraloid® B-72 is visible as a homogeneous film covering the ceramic surface, sealing some pores and cracks, and partially sealing other ones, keeping its permeability to humidity [5–7].

2.1.3. Radioactivity of the ceramic

This study was carried out in two steps:

– step one: according to [11,12], the raw-materials employed to manufacture ceramics, usually contain naturally occurring radionuclides, mainly U-238, Th-232 and K-40. In order to verify such occurrences in the *Macuxi* ceramic, 17 g of a powdered non-irradiated vessel, was analyzed in a high-resolution gamma spectroscope. The same radionuclides in concentrations very close to that ones, found in ordinary contemporary red ceramics were observed.

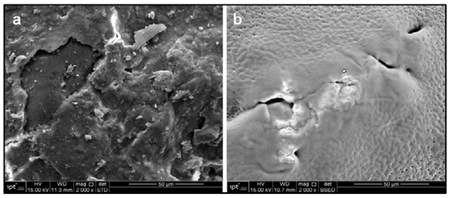

Fig. 3. Photographs of the ceramic fragments without (a) and with (b) Paraloid® B-72.

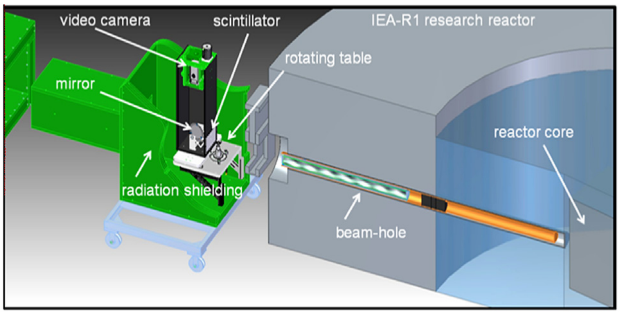

Fig. 4. Sketch of the equipment for neutron tomography.

– step two: to perform the tomography in the present equipment, the samples (ceramic vessels) are irradiated in an intense neutron beam (see 3.1), and radioactive activation of some of their chemical elements is expected. In order to determine the period, after irradiation, for which the induced radioactivity becomes negligible, 0.7 g of the same powdered vessel, was inserted in an aluminum holder and irradiated at the sample position for 400 s, the required time to obtain a tomography [13]. The powder was analyzed in a high sensitivity Ludlum (mod. 2929 dual scaler) counting system, which is able to detect alpha, beta and gamma radiations. The obtained result showed that approximately 30 h after the end of the irradiation, the level of counting of the irradiated ceramics became insignificant, as it reached the background level of counting system [14].

3. Penetration and distribution of paraloid® B-72

3.1. Neutron tomography

The equipment for tomography is installed at the Beam–Hole (BH) #14, of the 5MW IEA-R1 Nuclear Research Reactor, of IPEN-CNEN/SP (Brazilian Institute for Nuclear Technology). Fig. 4 shows the sketch of its main components: the rotating table where the vessels are irradiated; the scintillator screen (Li^6F/ZNS-NE426) where the image is formed; the plane mirror to reflect the image of the scintillator to the video camera; the CCD video camera (ANDOR ikon-M) for imaging capture; the radiation shielding. Furthermore two softwares, installed in a DELL (precision 5500) work station are used: Octopus V8.0 that from the captured images, generates tomographs (or slices) in the three viewing planes (XY, XZ, YZ), and VG Studio Max V2.2, which from the tomographs provides 3D images of the inspected vessel [15,16]. The neutron flux at irradiation position (measured by the Au-foil method) is 8×10^6 $n.s^{-1} \cdot cm^{-2}$, the maximal beam diameter is 16 cm, the best achievable spatial resolution is 205 ± 25 μm, the field of view is 18 × 18 cm^2, the L/D ratio is 104 ± 4, and the time spent per tomography is about 400 s. The Ref. [13] describe in detail, the equipment, and the procedures for tomography.

As already mentioned, two vessels, in which the consolidant was applied, at 40% RH and 90% RH, were tomographed. The penetration of Paraloid® B-72 was evaluated from the brightness level intensity

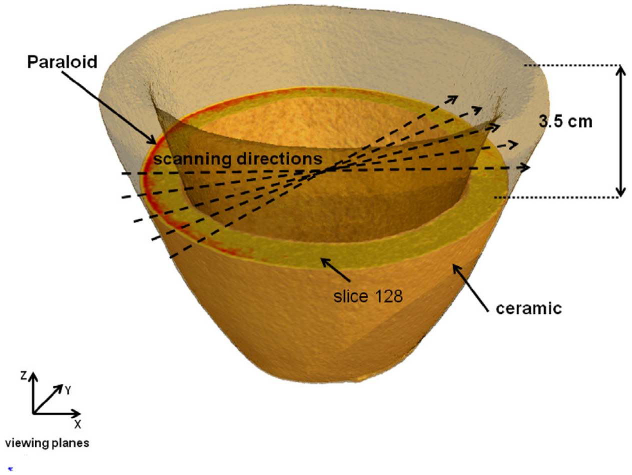

Fig. 5. Tomography slice — 128 for the vessel at 90% RH.

Table 1
Penetration of Paraloid® B-72 in the ceramic vessels.

Penetration of Paraloid® B-72	90% RH	40% RH
Depth at the highest concentration — (B–A)	1.1 ± 0.3 mm[*]	0.9 ± 0.3 mm[**]
Deepest penetration — (C–A)	3.4 ± 0.3 mm	3.9 ± 0.3 mm

[*] Gray Level $D = 36 \pm 3$.

[**] Gray Level $D = 33 \pm 3$.

distributions, obtained in a selected slice of the tomography, as a function of the scanning coordinate "x" along to the perpendicular direction to the vessel wall. The brightness level intensity was quantified in an 8 bit Gray Level (GL) scale ranging from 0 (darkest level) to 255 (brightest level), in such way that the greater is the (GL) value, the greater is the Paraloid® B-72 concentration [13].

Since the variations in the grain size, pore size, and the non-uniformity of the drying process affect the penetration of Paraloid® B-72 in the ceramic material, several distributions in different positions of the same slice, were determined.

For the vessel at 90% RH, twenty distributions in the slice 128, corresponding to the viewing plane XY, were obtained. Fig. 5 is a 3D image of this vessel showing the slice 128 at 3.5 cm from its surface, the Paraloid® B-72 is the semi-circular red ring at left, the ceramic body is the light brown, and the arrows indicate the directions in which the scans were obtained. A typically distribution is illustrated in Fig. 6 and consists of two distinct parts, the first to "Ceramic wall + Paraloid" and the second to "Ceramic wall". The twenty distributions were superimposed and the values of GL for each scanning coordinate were averaged. In this new distribution these two parts, were subtracted and the resulting net distribution of Paraloid® B-72 penetration in the vessel is shown in Fig. 7, which can be described as follows: the coordinate (A) represents the beginning of the vessel wall, where the Paraloid® B-72 was applied; the concentration of the consolidant continuously increases reaching its maximal at (B), for the Gray Level (D); as the depth increases, the concentration continuously decreases, reaching the deepest penetration at (C). Thus (B–A) is the depth in the vessel wall in which the Paraloid® B-72 reaches the maximal concentration and (C–A) is the deepest penetration. The obtained results are shown in Table 1. For the vessel at 40% RH, the same procedures were applied. The obtained distributions are illustrated in Figs. 8 and 9, and the respective results in Table 1.

The uncertainties in A, B, C and D are the mean standard deviations of their respective values corresponding to each one of the twenty individual distributions, and the uncertainties in (B–A) and (C–A) were evaluated by the standard propagation rules.

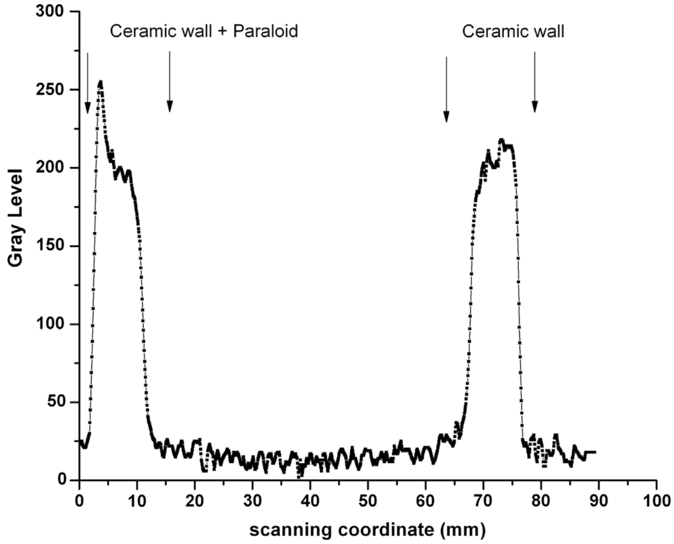

Fig. 6. Typical gray level intensity distribution for the vessel at 90% RH.

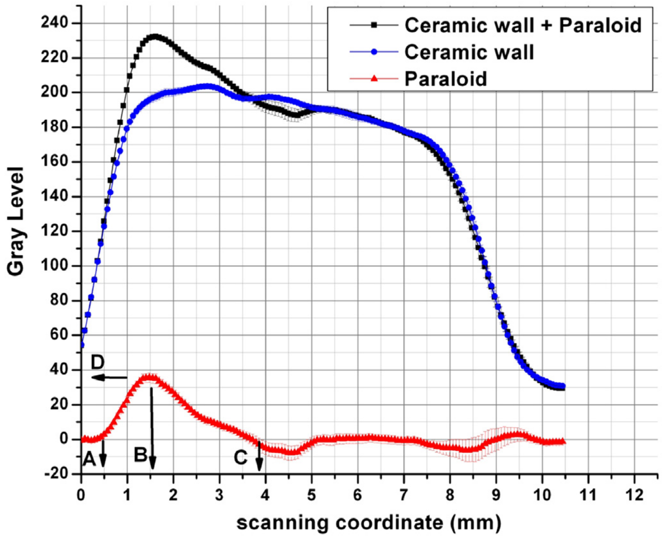

Fig. 7. Gray level distributions (black and blue) and the resulting net distribution (red) for the vessel at 90% RH.

3.2. 3D-neutron images

3D images have been applied since they provide a macro-visualization of the distribution of Paraloid® B-72 in the ceramic body. Firstly and for reference, Fig. 10(a) shows the 3D image of the entire vessel, as it is seen by the neutron beam. Fig. 10(b) and (c) show the consolidant distribution along the viewing plane XY in two regions, located at 13 mm and 18 mm from the vessel surface, corresponding to the slices 48 and 64 respectively. From these images, and because of the high sensitivity of neutrons to hydrogen (which is present in the Paraloid® B-72), it was possible to visualize the consolidant in the ceramic vessel, identify non-homogeneous impregnation regions, failure or regions in which Paraloid® B-72 was not absorbed, among others [17].

4. Conclusions

The results of Table 1 show that the penetration of Paraloid® B-72 in *Macuxi* ceramic is not affected by the humidity conditions of the vessels.

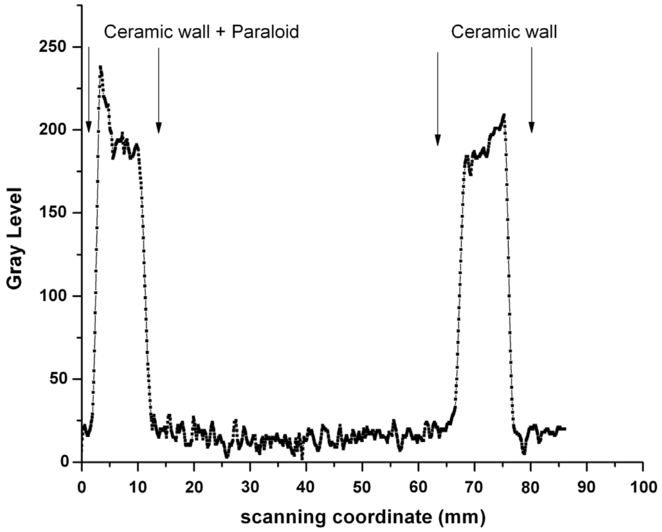

Fig. 8. Typical gray level intensity distribution for the vessel at 40% RH.

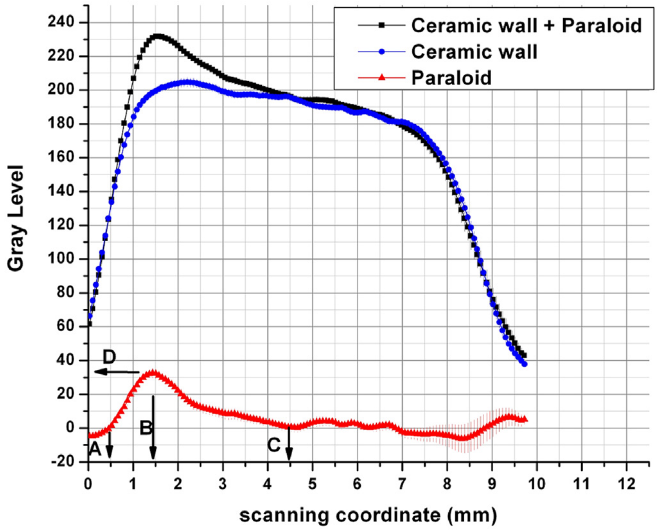

Fig. 9. Gray level distributions (black and blue) and the resulting net distribution (red) for the vessel at 40% RH.

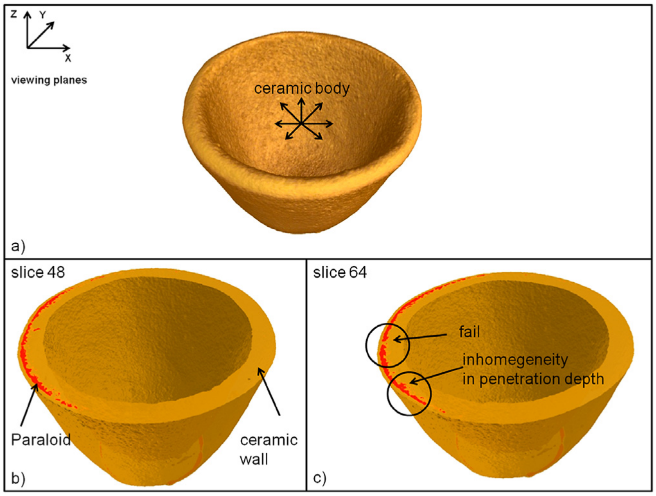

Fig. 10. 3D neutron images: (a) entire vessel; (b) and (c) distribution of the consolidant in two distinct regions of the ceramic vessel.

The thicknesses of the vessel walls vary between 5 mm to 9 mm and since the maximal penetration of Paraloid® B-72 is about 3.4 ± 0.2 mm for the vessel kept at 90% RH and of 3.9 ± 0.2 mm for the vessel at 40% RH, no part of the vessels is entirely protected.

Fig. 10 demonstrated the importance of 3D images for the present study since they allow a macro-visualization of the distribution of Paraloid® B-72 in the ceramic body, in any region of the three viewing planes "XY", "XZ", "YZ", or eventually in the entire vessel at once.

Another very important aspect verified was the radioactivity of the ceramic. The results showed although the raw-materials contain naturally occurring radionuclides, the neutron-induced radioactivity becomes negligible approximately 30 h after the end of the tomography procedure.

Considering that the studied vessels were manufactured by an indigenous artisan according to the same procedures used by their ancestors, the obtained results can serve as a guide to extrapolate the behavior of Paraloid® B-72 to other archeological ceramic objects from this same region.

Acknowledgments

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References

[1] Nuclear techniques for cultural heritage research, IAEA Radiation Technology Series No. 2.
[2] O.A. Derby, The artificial mounds of the Island of Marajo, Brazil, Amer. Nat. 13 (4) (1879) 224–229.
[3] F.A. Silva, Loiça de barro do agreste: um estudo etnoarqueológico de cerâmica histórica pernambucana (M.Sc. thesis), University of São Paulo, Brazil, 2012.
[4] C. Constâncio, L. Franco, A. Russo, C. Anjinho, J. Pires, M.F. Vaz, A.P. Carvalho, Studies on polymeric conservation treatments of ceramic tiles with Paraloid B-72 and two alkoxysilanes, J. Appl. Polym. 116 (2010) 2833–2839.
[5] G. Fleischer, J. Nimmrichter, A. Rohatsch, The relevance of scientific investigation for the preservation of monuments and historic buildings made of stone e a state of the art report, Geophys. Res. Abstr. 7 (2005) SRef-ID: 1607e7962/gra/EGU05-A-04479.
[6] E. Carreti, L. Dei, Physicochemical characterization of acrylic polymeric coating porous materials of artistic interest, Prog. Org. Coat. 49 (2004) 282–289.
[7] M.I. Prudêncio, M.A. Pereira Stanojev, J.G. Marques, M.I. Dias, L. Esteves, C.I. Burbidge, M.J. Trindade, M.B. Albuquerque, Neutron tomography for the assessment of consolidant impregnation efficiency in portuguese glazed tiles (16th and 18th centuries), J. Archaeol. Sci. 39 (2012) 964–969.
[8] T.P. Santos, M.F. Vaz, M.L. Pinto, A.P. Carvalho, Porosity characterization of old Portuguese ceramic tiles, Constr. Build. Mater. 28 (2012) 104–110.
[9] https://pib.socioambiental.org/pt/povo/macuxi/734. (Accessed August 2017).
[10] M.F. Vaz, J. Pires, A.P. Carvalho, Effect of impregnation treatment with Paraloid B-72 on the properties of old Portuguese ceramic tiles, J. Cult. Heritage 9 (2008) 269–276.
[11] http://nvlpubs.nist.gov/nistpubs/Legacy/TN/nbstechnicalnote1118.pdf. (Accessed July 2016).
[12] http://nucleardata.nuclear.lu.se/toi/perchart.htm. (Accessed February 2017).
[13] R. Schoueri, C. Domienikan, F. Toledo, M.L.G. Andrade, M.A. Pereira Stanojev, R. Pugliesi, The new facility for neutron tomography of IPEN-CNEN/SP and its potential to investigate hydrogenous substances, Appl. Radiat. Isot. 84 (02/2014) (2014) 22–26.
[14] Nuclear Energy National Commission, Basic Guidelines for Radiation Protection, CNEN, Rio de Janeiro, 2014 (CNEN NN 3.01).
[15] https://www.octopus.be/nl. (Accessed September 2017).
[16] https://www.volumegraphics.com/. (Accessed September 2017).
[17] J. Rant, Z. Milic, J. Istenic, T. Knific, I. Lengar, A. Rant, Neutron radiography examination of objects belonging to the cultural heritage, Appl. Radiat. Isot. 64 (1) (2006) 7–12.