Characterization of the lime mortars of Rui Barbosa House Museum in Rio de Janeiro - Brazil

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ABSTRACT: The aim of this research is to characterize the mortars of the Rui Barbosa House Museum, built in 1850, in the city of Rio de Janeiro, Brazil, using X-ray diffraction (XRD), gel-CSH determination, Fourier Transform Infrared spectrometry (FTIR), Wavelength-Dispersive X-ray Fluorescence spectrometry (WDXRF), Thermo gravimetric analysis (TG-DTG) and granulometric analysis. Also, petrographic and physical characteristics such as porosity, water absorption and apparent density of the mortars were used to identify the raw materials employed in their preparation. Mineralogical associations found are similar (quartz, calcite, kaolinite, microcline, muscovite and albite) for the majority of samples and only vary in their proportions; the most prominent phases are quartz and calcite. The collected data, indicating that the binder is hydrated lime, lead us to conclude that the analyzed samples are lime mortars, discounting the possibility of cement as the binder material. Two samples, located on the corner of the building, which underwent repairs, present a differentiated behavior, with high levels of dolomite and the presence of pozzolanic material, with greater water absorption and higher density, indicating the use of a different mortar type. In addition, it was verified that the WDXRF and XRD methods are able to determine the trace element composition with comparable precision with respect to the methodological approach proposed by Teutonico (1988). In addition, it has been verified that the major pollutant causing degradation of building are sulfur emitted by the vehicles and saline spray.

1 INRODUCTION

1.1 Mortars

Mortar is a workable paste used to bind masonry blocks together and fill the gaps between them. Typically the historical mortar is a composite, with binder and aggregate (Chiari et al., 1992). Gypsum is one of the oldest binders used by humanity, it was employed in the first Egyptian pyramids (Como, 2013) and recently the presence of gypsum was reported in most samples of a church, founded between the fourth and fifth century, at the end of the period when Milan was the capital of the Roman Empire (Bertolini et al., 2013). Mortars with other components such as lime and whale oil have appeared over the years, thus improving the properties of this material (Bertolini et al., 2013; Chiarelli et al., 2015; Gleize et al., 2009; Maria, 2010).

The use of lime mortar in Brazil predates the foundation of Salvador city (Bahia) in 1549, as it since the period of the Hereditary Captaincies. Since its first use in Brazil all the lime was prepared from rocks, lioz stones (limestones) as in Lisbon, provided by Portugal (Santiago, 2012). However, abundance sources of corals were discovered along the Brazilian coastline and shortly served as an excellent substitute, generating high quality lime (Santiago, 2012).

Lime was the most common binder and could typically be found in construction, manufacturing and material coating processes until the beginning of nineteenth century. From this period, with the discovery of Portland cement, the binder has fallen into disuse, compared to some ad-
vantages offered by cement, such as rapid hardening, high mechanical strength and the possibility of use associated with steel in the confection of structural elements such as slabs, beams and pillars (Santiago, 2012).

The characterization of the mortars is very important because it enables a future preparation of mortars with similar properties to those originally used in the construction of historical buildings. Several places in the world have already had their mortars characterized, including those from the Byzantine period, from the sixth to the tenth centuries (Bakolas et al., 1998).

Many techniques have been successfully applied in the characterization of historical mortars, for example, X-ray diffraction (Moropoulou et al., 1995; Moropoulou et al., 2000; Biscontin et al., 2002; Freidin, 2005; Zeng, 2008; Adrano, 2009; Budak, 2010; Sanjurjo et al., 2010, and Martinez, 2013), macroscopic observation (Lezzerini et al., 2014), petrography (Leone et al., 2016), physical properties (Leone et al., 2016), infrared spectroscopy (Bakolas et al., 1998), chemical analysis (Lezzerini et al., 2014), thermogravimetric analysis (TG-DTG) (Martinez, 2013; Lezzerini et al., 2014), mechanical tests (Moropoulou, 2003) and granulometry (Bakolas et al., 1998; Lezzerini et al., 2014).

In this research, the composition and physical properties of mortars taken from Rui Barbosa House Museum was evaluated by X-ray diffraction, petrographic analysis, Raman Spectroscopy, Wavelength-Dispersive X-ray Fluorescence spectrometry, Fourier Transform Infrared spectrometry, thermo gravimetric analysis (TG-DTG) and granulometric and physical analysis to confirm or discard the presence of cement and gypsum as binder materials.

1.2 Rui Barbosa House Museum

Rui Barbosa House Museum (Figure 1) was built in 1850 with neoclassical architecture and is located in the southern of the city of Rio de Janeiro in Rio de Janeiro State, Brazil, about 1 km away from Guanabara Bay (22°56'57.1"S 43°11'13.3"W) (GOOGLE, GOOGLE MAPS (2016). The Museum has historical and cultural importance to Brazilians, it is part of the Rui Barbosa House Foundation (Ministry of Culture - Brazil) and it was one of the firsts historic house museums in Brazil. The building was the residence of Ruy Barbosa de Oliveira who among other duties was a lawyer, a writer and a politician of great importance to Brazil (www.casaruibarbosa.gov.br, access on may 2016).

Figure 1: Façade of Rui Barbosa House Museum.
2. MATERIALS AND METHODS

2.1. Sampling

Twelve mortars samples were taken from the façade of the Rui Barbosa House Museum (Figure 2).

(i) S-001 to S-004: four samples of south side (main façade).
(ii) S-005 to S-007: three of east side.
(iii) S-008 to S-010: three of north side.
(iv) S-011 and S-012: two samples of west.

2.2. Methods

The samples were first observed macroscopically, for characteristics that can be identified by
the naked eye, such as color, texture, shape and size.

The mortars studied were described using a magnifying glass Schneider, with a Carl Zeiss
lens, zoomed in from 6.5 to 60X and fluorescent light. The Raman analyses were carried out, to
support the observation, using a BWTEK Raman device. The equipment covers a spectral range
in Raman displacement of 150-3000 cm\(^{-1}\), with a spectral resolution of 5 cm\(^{-1}\). Spectra were
acquired using commercial software provided by BWTEK.

Some samples were separated for physical analysis and preparation of slides to petrographic
analysis and the remainder was fractionated manually ground with an agate pestle and passed
through a sieve up to 105µm and characterized using X-ray powder diffraction (XRPD), Fourier
transform infrared spectrometry (FTIR) and wavelength-dispersive x-ray fluorescence spectrometry (WDXRF).

X-ray diffraction results were recorded on a Bruker D4-Endeavor instrument (40 kV, 40 mA)
with a CoKα wavelength, from 10 to 100° in 2θ, step size of 0.02° and 3.6 s/step scan.

Fourier transform infrared spectrometry (FTIR) used was Perkin Elmer model Spectrum 400
for the qualitative identification of compounds present in the mortars, such as salts and organic
composites. The pellets were 13 mm in diameter contained approximately 2.0% of the sample;
they were well mixed of 300 mg potassium bromide.

Samples for observations under optical microscopic were prepared using vacuum impregna-
tion with an epoxy resin during a period of 40 hours. These were observed through a binocular
petrographic microscope and polarized to transmitted light, with the objective of increase of 2.5
to 60 times, Carl Zeiss microscope. The identification of minerals followed the principles of optical mineralogy and petrography: color, extinction angle, characteristics and properties observed using conoscopic illumination.

The WDXRF samples were dried in oven at 100°C and 7 g of each sample were pressed into uniform pellets of 20 mm diameter using the Vaneox automatic press machine under 20 tons of pressure with a standing time of 30 s, using boric acid as binder. All the measurements were carried out on an AXIOS Panalytical WDS-1 spectrometer. The loss on ignition (LOI) was detected using Lecco TGA-701 equipment, with 10°C.min-1 at 25-110°C and 40°C.min-1 at 110-1000°C.

Apparent density, porosity and water absorption was measured at atmospheric pressure by Marte model AD2000 hydrostatic balance on the water-saturated samples and the dried samples on Shimadzu model AY220.

1. RESULTS AND DISCUSSION

3.1. Macroscopic description, observation and Raman spectroscopy

The mortars samples (Figure 3a) analyzed present similar aspects. They are all constituted by a thin matrix with visible mineral grains, many of them are identifiable as quartz, whose coloration varies from milky to colorless with various shapes, but mainly elongated. Another element observed, visible to the naked eye, was spherical grains with rounded edges, slightly pink, possibly potassic feldspars. There were some air voids in all samples.

Based on cohesion and color characteristics the analyzed samples (Figure 3) can be divided into two groups one with more cohesive matrix S-002, S-003, S-005, S-006 and S-012 with aggregates well adhered and coherent. The matrix has light color (beige to grey) and the occurrence of well dispersed lime lumps is frequent. It was observed dispersed in the binder a mineral with ochre color; and identified as plagioclase by a Raman analysis. The occurrence of staining by ferric oxide was seen in all samples, usually associated to plagioclase. In the sample S-006 it was seen the presence of garnets, one of them very degraded and showing ochre staining.

The second group is composed by samples S-007, S-008, S-009 and S-011, where the matrix are relatively darker (brownish) and present a powdery aspect, more evidently in S-007.

In samples S-012 (Figure 3b) and S-008 was observed the presence of a wood piece. During the sampling was observed, in a few regions, detachment of the ink layer from the walls of the building, but no other sign of chemical or biological degradation.

(a) General aspect of the mortars (S-007). Presence of wood in the mortar (S-012).

Figure 2: Samples of the mortars

Different from all other samples, S-001 has light pink matrix, with some areas pale yellow. The aggregate has small grain size, still abundant quartz, angle-shaped, but smaller and in minor quantity when compared to the others samples. The presence of shell pieces is more frequent. This mortar is heavier and more coherent, very distinct visually from the rest.
3.2. Mineralogical and petrographic characterization

3.2.1 Mineralogical analysis

The mineralogical analysis by XRPD analysis (Table 1) indicated that quartz is the main component of the binder and the second most abundant component is calcite. Kaolinite, phyllosilicates (muscovite) and K-feldspars (microcline) are present in smaller amounts. Traces of albite were found in most of the samples analyzed. No amorphous nature was detected with the X-ray diffraction technique. Ettringite and portlandite are also absent in the samples. Therefore, the mortars of Rui Barbosa House Museum are composed by, mainly, siliceous aggregates and calcitic lime binder.

Table 1: Mineralogical composition of the mortars assessed by XPRD.

<table>
<thead>
<tr>
<th>Sample</th>
<th>quartz</th>
<th>calcite</th>
<th>kaolinite</th>
<th>microcline</th>
<th>muscovite</th>
<th>albite</th>
</tr>
</thead>
<tbody>
<tr>
<td>S-001</td>
<td>+++</td>
<td>+++</td>
<td>t</td>
<td>+</td>
<td>+</td>
<td>t</td>
</tr>
<tr>
<td>S-002</td>
<td>+++</td>
<td>++</td>
<td>++</td>
<td>++</td>
<td>+</td>
<td>t</td>
</tr>
<tr>
<td>S-003</td>
<td>+++</td>
<td>++</td>
<td>++</td>
<td>++</td>
<td>+</td>
<td>t</td>
</tr>
<tr>
<td>S-004</td>
<td>+++</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>t</td>
</tr>
<tr>
<td>S-005</td>
<td>+++</td>
<td>++</td>
<td>t</td>
<td>+</td>
<td>t</td>
<td>-</td>
</tr>
<tr>
<td>S-006</td>
<td>+++</td>
<td>++</td>
<td>++</td>
<td>+</td>
<td>+</td>
<td>t</td>
</tr>
<tr>
<td>S-007</td>
<td>+++</td>
<td>++</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>t</td>
</tr>
<tr>
<td>S-008</td>
<td>+++</td>
<td>++</td>
<td>+</td>
<td>+</td>
<td>++</td>
<td>t</td>
</tr>
<tr>
<td>S-009</td>
<td>+++</td>
<td>+</td>
<td>-</td>
<td>t</td>
<td>t</td>
<td>-</td>
</tr>
<tr>
<td>S-010</td>
<td>+++</td>
<td>++</td>
<td>-</td>
<td>t</td>
<td>+</td>
<td>t</td>
</tr>
<tr>
<td>S-011</td>
<td>+++</td>
<td>+</td>
<td>-</td>
<td>-</td>
<td>t</td>
<td>t</td>
</tr>
<tr>
<td>S-012</td>
<td>+++</td>
<td>+</td>
<td>t</td>
<td>t</td>
<td>+</td>
<td>t</td>
</tr>
</tbody>
</table>

Notation: +++ (abundant); ++ (present); + (small amount); t (traces); - (undetected)

3.2.2 Petrographic analysis

The petrographic analysis by microscope helps to identify the aggregate types, their morphology, alteration state, and the relation between aggregate and binder. The aggregates are mainly composed of polycrystalline quartz and K-feldspars.

The pores observed in mortars have irregular shapes and size. In sample S-001 it is identified a mortar with very thin matrix (Figure 4a), mostly in beige or pink color in some parts gets dark brown (Figure 4b). Some round holes can be seen, which can suggest empty spaces left by probably during the lamination process. The aggregate presents mostly angle-shaped quartz, in milimetre sizes, well dispersed in the matrix. There are feldspars as well, and some very small muscovites and biotites are present.

Ochre staining can be seen around some minerals (Figure 4c). An important aspect of this sample compared to all the others is the presence of shell pieces (Figure 4d) in different shapes and sizes.
The other mortar are basically pretty similar, they all have brown matrix, angle-shaped quartz dispersed in matrix, as well as feldspar and some biotites (Figure 5). It is possible to see some carbonate grains and an irregular porosity. In sample S-007 the porosity seems more evident, and perhaps it is related to its macroscopic appearance.

3.3. Chemical characterization

3.3.1. WDXRF analysis

SiO₂ (33.20 to 70.00% wt) and CaO (6.10 to 29.20% wt) are the most abundant components of WDXRF analysis as reported at the Table 2. Samples contain SiO₂/ CaO ratio (wt%) between 1 and 4, that is, sample S-001 has 1:1, SiO₂: CaO, respectively, while samples S-007, S-009 and S-011 showed values of 1: 4. The exceptions were only samples S-008 and S-010, both of the North side.

The percentages of Na₂O and MgO were below 2% in all analyzed samples. The average values of aluminum oxide (Al₂O₃) were 7%, only sample S-009 presented less than 4. Ti-
nium oxide (TiO₂) was detected in all samples with values below 0.4%. The SO₃ content is low in all the samples, up to 1%.

The WDXRF results confirmed X-ray diffraction results, as follows:
In most samples the main component is quartz.
Showing that all samples contain high percentage of quartz and calcite.
Lower amounts and traces of kaolinite, microcline, muscovite and albite.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Side</th>
<th>Na₂O</th>
<th>MgO</th>
<th>Al₂O₃</th>
<th>SiO₂</th>
<th>K₂O</th>
<th>CaO</th>
<th>TiO₂</th>
<th>Fe₂O₃</th>
<th>LOI</th>
</tr>
</thead>
<tbody>
<tr>
<td>S-001</td>
<td>South</td>
<td>0.64</td>
<td>0.80</td>
<td>10.70</td>
<td>33.20</td>
<td>1.80</td>
<td>29.20</td>
<td>0.29</td>
<td>2.50</td>
<td>19.70</td>
</tr>
<tr>
<td>S-002</td>
<td>South</td>
<td>0.69</td>
<td>0.43</td>
<td>7.60</td>
<td>58.40</td>
<td>1.80</td>
<td>18.80</td>
<td>0.13</td>
<td>1.20</td>
<td>10.30</td>
</tr>
<tr>
<td>S-003</td>
<td>South</td>
<td>0.92</td>
<td>0.42</td>
<td>7.70</td>
<td>56.00</td>
<td>2.00</td>
<td>19.60</td>
<td>0.14</td>
<td>1.50</td>
<td>10.60</td>
</tr>
<tr>
<td>S-004</td>
<td>South</td>
<td>0.73</td>
<td>0.55</td>
<td>7.56</td>
<td>55.40</td>
<td>2.00</td>
<td>18.90</td>
<td>0.13</td>
<td>1.40</td>
<td>10.40</td>
</tr>
<tr>
<td>S-005</td>
<td>East</td>
<td>0.38</td>
<td>0.75</td>
<td>6.10</td>
<td>46.30</td>
<td>1.10</td>
<td>26.50</td>
<td>0.18</td>
<td>1.50</td>
<td>15.80</td>
</tr>
<tr>
<td>S-006</td>
<td>East</td>
<td>0.79</td>
<td>0.50</td>
<td>4.90</td>
<td>61.00</td>
<td>1.10</td>
<td>19.50</td>
<td>0.12</td>
<td>0.78</td>
<td>10.20</td>
</tr>
<tr>
<td>S-007</td>
<td>East</td>
<td>0.97</td>
<td>0.40</td>
<td>8.10</td>
<td>61.00</td>
<td>1.90</td>
<td>16.10</td>
<td>0.15</td>
<td>1.30</td>
<td>9.30</td>
</tr>
<tr>
<td>S-008</td>
<td>North</td>
<td>1.90</td>
<td>0.59</td>
<td>15.30</td>
<td>64.80</td>
<td>3.60</td>
<td>6.10</td>
<td>0.24</td>
<td>1.70</td>
<td>5.10</td>
</tr>
<tr>
<td>S-009</td>
<td>North</td>
<td>0.19</td>
<td>0.48</td>
<td>1.80</td>
<td>70.00</td>
<td>0.30</td>
<td>16.00</td>
<td>&lt;0.10</td>
<td>0.42</td>
<td>10.10</td>
</tr>
<tr>
<td>S-010</td>
<td>North</td>
<td>0.94</td>
<td>1.30</td>
<td>9.30</td>
<td>69.30</td>
<td>2.00</td>
<td>8.60</td>
<td>0.36</td>
<td>1.60</td>
<td>5.40</td>
</tr>
<tr>
<td>S-011</td>
<td>West</td>
<td>0.96</td>
<td>0.36</td>
<td>6.90</td>
<td>60.30</td>
<td>1.60</td>
<td>16.10</td>
<td>0.11</td>
<td>1.10</td>
<td>11.70</td>
</tr>
<tr>
<td>S-012</td>
<td>West</td>
<td>0.82</td>
<td>0.32</td>
<td>6.60</td>
<td>70.00</td>
<td>1.60</td>
<td>12.10</td>
<td>0.11</td>
<td>1.10</td>
<td>7.00</td>
</tr>
</tbody>
</table>

3.3.2. FTIR analysis

Through analysis of FTIR spectra of samples, reported in Figure 6, is possible to observe that samples of the four sides of Museum present the same behavior. The presence of bands of calcium carbonate (1430, 873 and 712 cm⁻¹) corroborating with the loss on ignition analysis. The characteristic silicate band (Si-O-Si) appears close to 1030 cm⁻¹ (Genestar et al., 2006; Rodrigues, 2010). It is worth mentioning that these analyzes confirmed X-ray diffraction and X-ray fluorescence results which indicate that the samples are composed mostly of quartz (1874, 1072, 794, 695 cm⁻¹) and calcite (1796, 1430, 874, 713 cm⁻¹), containing small amounts of kaolinite (535 cm⁻¹), albite (778 cm⁻¹) and microcline (648 cm⁻¹) (Saikia and Parthasarathy, 2010; Sivakumar, et. al, 2010; Sivakumar et al., 2012). Organic compounds and hydrate salts were not detected.

Figure 5: FTIR spectras at samples S-001, S-005, S-008, and S-011.

3.4 Physical properties of the mortars

The values of the physical properties that are highly dependent on the amount of voids such as porosity and water absorption at atmospheric pressure of the mortars are reported in Figure 7. The porosity of samples varies between 14 and 33% and the water absorption between 7 and 21% by weight. Lezzerini and co-workers reported water absorption at the atmospheric pressure
of the examined mortars a range between 11 to 23 % and porosity 25 to 40%. (Lezzerini et al, 2014). In the physical properties, the south and west sides have very similar behavior in the analyses performed. While the east and north have higher values for total porosity and water absorption than the others, however, these two sides presented similar results among themselves.

Figure 6: Total porosity and water absorption at atmospheric pressure with standard deviation of the samples.

Figure 8 shows the apparent density of the samples; dry versus water-saturated apparent density with average values of 1761 kg.m⁻³ and 1993 kg.m⁻³, respectively. Lezzerini and co-workers reported values for apparent density between 1570 and 2010 kg.m⁻³. Therefore, all samples from the Museum presented apparent density values compatible with those reported in the literature (Lezzerini et al, 2014).

Figure 7: Apparent density of the mortars samples with standard deviation.

4. CONCLUSIONS

Mortars are extremely complex materials and a lot of recipes of ancient mortars are present. In this research, the mortars from the facade of the Rui Barbosa House Museum (Rio de Janeiro, Brazil) were analyzed. The chemical composition of the analyzed mortars shows a high percentage of silica (greater than 50% w.t.). In addition to dominant quartz and calcite, phyllosilicates (kaolinite and muscovite) and K-feldspars (microcline) are present in smaller amounts. Furthermore, traces of albite were found in most of the samples analyzed. Organic compounds and hydrate salts were not detected. It was possible to determine, by the naked eye, the presence of wood fragments and shell pieces, which were seen under the microscope as well. The results indicate that these are mainly lime mortar, and that neither gypsum nor cement was used as binder; in fact, no traces of gypsum, ettringite or portlandite were detected by X-ray diffraction analysis.
Two, the samples (S-002 and S-005) present different features with respect to the other mortars: the first is the only sample consisting of pozzolanic material and lime, while the second is the only one that contains very abundant dolomite, which makes this mortar more adhesive than all the others. These two samples have been taken from building corners, which may be easily damaged by people passing by. Therefore, these portions of the façade are not original and probably underwent frequent repairs the differences in the mortars' chemical, mineralogical and physical features may indicate that, during repairs, no attention was paid to reproduce the original mortars of the façade.

We also suggest that the XRPD and WDXRF techniques are capable of determining the reconstitution of mortar with precision in a shorter time than the method proposed by Teutonico (1988).

The results related to the effects of pollutants indicate that the building is affected significantly by the action of the sulfur emanated by the vehicles that circulate around and by the action of the saline spray, since the location of the building is at a small distance (less than 2 km) from the sea.

5. ACKNOWLEDGEMENTS

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