Characterization of Ornamental Stones Wastes for Use in Ceramic Materials

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Abstract. Ornamental stones processing produces large amounts of wastes, which without treatment, are disposed in deposits, constituting the major environmental problem in this sector in Brazil. There is a great variety of rocks and different technologies in the ornamental stones processing. Rock block sawing can be performed using multi-blade gangsaw, the conventional technology, or multiwire gangsaw, latest technology which uses only diamond wire and water to cut blocks. In recent years there has been a great change in the use of ornamental stones sawing technologies, where currently almost 50% of the sawed materials are processed by the multi wire technology. The ornamental stones wastes have compounds that can collaborate in the processing of the ceramic. Due to the great variety of Brazilian ornamental stones and technologies in addition to the growth of the sector in recent years, there is a need for new studies regarding the characterization and environmental classification of waste, for a better management and application. Therefore, the objective of this work was the characterization and environmental classification of ornamental stones wastes aiming their use in red ceramics. The wastes were characterized with the determination of its chemical composition and mineralogical analysis, particle size, morphological analysis and environmental, the latter by means of the leaching and solubilization tests, for subsequent classification. The wastes are composed mainly of SiO₂, Al₂O₃, alkaline oxides, earth alkaline oxides and iron, and those which were submitted to the leaching and solubilization tests are classified as non-inert.

Introduction

Brazil is one of the main producers and exporters of ornamental stones in the world [1], and the State of Espírito Santo is the national leader in the production and processing of rocks. In 2016, 9.3 million tons of ornamental stones were produced in Brazil [2], generating a large amount of waste. It is estimated that approximately 2 million tons of fine residues per year are generated in Brazil, with 1.5 Mt in the state of Espírito Santo [3].

The productive chain of the ornamental stone sector is divided into extraction and processing, which the second is subdivided into sawing and polishing. In the extraction, the block is quarried from the rocky mass and then transported to the sawing process, where it occurs the cutting of the block in slabs, by the multi-blade or multi wire gangsaw. A procedure recently incorporated to the processing of the most fragile blocks is the enveloping, in which a fiberglass and resin blanket is used to envelop the blocks up before they be sawed, increasing the resistance of mechanical stresses. In the polishing occurs the closing of the pores of the slabs and will be conferred the brightness to the surface.

Multi-blade sawing, conventional technology, performs the cutting of the block in slabs using steel blades, with the aid of a compound of water, steel-grit and lime and/or bentonite for the sawing of the blocks. The multi wire sawing, latest technology uses only diamond wire and water for cutting blocks. The sludge from processing is directed to the filter press to separate the water, which will be utilized in the production process, from the solid particles.
In the production of ornamental stones the waste that generates greater concern is the one coming from the processing of the rocks. This process generates a large amount of wastes which might contain elements or compounds that can classify them as non-inert.

The State Institute of Environment and Water Resources - IEMA of Espírito Santo, normative instruction nº 11-2016, Annex II, established a permanent Program for the characterization of the residue of Sludge of the Ornamental Stones Processing (Lama do Beneficiamento de Rochas Ornamentais - LBRO, in portuguese) requiring that landfills, used for this purpose, should present a LBRO Characterization Report, based on the methodologies described in NBR 10004 [4].

Due to the great variety of Brazilian ornamental stones and technologies in addition to the growth of the sector in recent years, there is a need for new studies regard to the characterization and environmental classification of waste, for a better management and application. Therefore, this work had as objective the characterization and environmental classification of ornamental stones wastes aiming their use in red ceramics.

Materials and Methods

The wastes studied in this work were collected in ornamental stone industries in the State of Espírito Santo, in Brazil, coming from the multi wire gang saw sawing process (called MWE and MWC), from the multi-blade gangsaw sawing process (MBE) and from the filter press (MBF), which contains wastes from sawing and polishing processes. The wastes MWE and MWC come from the yellow granite and of black granite sawing process, respectively, and the wastes MBE and MBF are from the processing of several rocks.

Sampling was performed according to the solid waste sampling standard NBR 10007 [5]. The wastes were dried in the oven at 110 °C for 24 hours, once they were deagglomerated and quartered by an elongated stack and Jones quarter the samples were prepared for the characterization. It was carried out the chemical, physical, mineralogical, morphological and environmental characterization of the wastes. X-ray diffraction (XRD), chemical analysis, particle size distribution and scanning electron microscopy (SEM) analyzes were performed. For the XRD assays, samples were passed at 74 μm sieve (200 mesh).

The chemical composition was determined by X-ray fluorescence (XRF) in a Spectrometer WDS model AXIOS from Panalytical and the loss by calcination in a Leco TGA-701 equipment. The mineralogical analysis was conducted by X-ray diffraction (XRD) in a D4 model Endeavor Bruher diffractometer coupled with a Goebel mirror for parallel beam. The XRD operation was carried out with CoKα radiation with the 20 angle ranging from 5 to 80°. The wastes particle size distribution was determined using the Mastersizer 2000 equipment, from Malvern Instruments. Micrographs were obtained by SEM using the FEI Quanta 400 microscope.

In order to verify the mobility of pollutants, leaching and solubilization tests, according to NBR 10005 [6] and 10006 [7], were performed in two types of wastes, the MWE and MBF. The elements, as well as other substances required by standard NBR 10004 [4], were determined in the solubilization and leaching extracts.

Results and Discussion

Table 1 shows the chemical composition and loss by calcination of the wastes. The main components of the wastes are SiO₂, followed by Al₂O₃ and alkaline oxides (Na₂O and K₂O), earth alkaline oxides and iron.

Wastes from ornamental stones processing using multiblade gangsaw showed higher Fe₂O₃ contents due to the use of blades and steel-grits. MWC waste presented high iron content due to the composition of the sawn rock. One advantage of the waste MWE is its low Fe₂O₃ content (1.20%). MWE waste was the one with the highest amount of SiO₂, which is probably associated with quartz, feldspar, micaeous minerals, as confirmed by X-ray diffractograms, Fig. 1. The inert quartz in the waste contributes to a reduction in the plasticity of the clayey body and the retraction of ceramics, in addition, in some cases, increases refractoriness, also the quartz particles may impair the
mechanical strength of the final ceramic [8]. The alkaline oxides present in the wastes can act as a fluxing agent and contribute to the ceramic sintering [8]. MWE waste was the one with the highest amount of flux oxides. MBF waste was the one that presented the highest loss by calcination. The high loss of the waste can cause the formation of pores in the ceramic and a very low indicates a thermal stability. The composition of the wastes varies due to the composition of the rocks, of the processing, the inputs used and the water treatment process.

The chemical composition and loss by calcination results of the wastes studied are in agreement with the found in literature [9, 10].

Table 1: Chemical composition and loss by calcination of the wastes (wt. %).

<table>
<thead>
<tr>
<th>Waste</th>
<th>SiO₂</th>
<th>Al₂O₃</th>
<th>Fe₂O₃</th>
<th>K₂O</th>
<th>Na₂O</th>
<th>CaO</th>
<th>MgO</th>
<th>TiO₂</th>
<th>P₂O₅</th>
<th>SO₃</th>
<th>BaO</th>
<th>MnO</th>
<th>Loss by calcination</th>
</tr>
</thead>
<tbody>
<tr>
<td>MWE</td>
<td>75.1</td>
<td>14.7</td>
<td>1.2</td>
<td>4.3</td>
<td>2.9</td>
<td>0.8</td>
<td>0.3</td>
<td>0.1</td>
<td>0.1</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.3</td>
</tr>
<tr>
<td>MWC</td>
<td>53.0</td>
<td>20.8</td>
<td>6.2</td>
<td>0.9</td>
<td>4.1</td>
<td>5.4</td>
<td>4.7</td>
<td>1.9</td>
<td>1.6</td>
<td>0.2</td>
<td>1.0</td>
<td>0.1</td>
<td>1.6</td>
</tr>
<tr>
<td>MBF</td>
<td>65.2</td>
<td>17.5</td>
<td>3.7</td>
<td>2.2</td>
<td>4.1</td>
<td>3.4</td>
<td>1.2</td>
<td>0.5</td>
<td>0.4</td>
<td>0.1</td>
<td>0.2</td>
<td>0.1</td>
<td>5.1</td>
</tr>
<tr>
<td>MBE</td>
<td>62.2</td>
<td>17.0</td>
<td>4.7</td>
<td>1.9</td>
<td>3.4</td>
<td>4.6</td>
<td>2.6</td>
<td>0.9</td>
<td>0.8</td>
<td>0.1</td>
<td>1.6</td>
<td>0.1</td>
<td>2.6</td>
</tr>
</tbody>
</table>

Fig. 1 shows XRD pattern of the studied wastes. The same crystalline phases were identified in the wastes, being quartz (SiO₂), albite (NaAlSi₃O₈), microcline (KAlSi₃O₈) and mica, with different intensities. Microcline and albite can act as fluxes during ceramic sintering. Quartz acts as a non-plastic material in the water/clay system. During burning, the quartz can act as inert and contribute to the generation of micro cracks in the material. Mica is a group of minerals mainly composed of hydrated silicates; among them is the biotite and muscovite.

Table 2 shows the results of the particle size distribution of the wastes. In this table, it is possible to notice that the waste present about 10% of the particles a very fine particle size, close to 2 µm d(0.1), with the exception of the MWC waste. Particles below 2 µm correspond to clay fraction. It
can be seen that 50% of the wastes particle are below 20 µm d(0.5), with the exception of the MWC waste. Particles from 2 to 20 µm correspond to the silt fraction. It is also observed that the MBE waste presented the highest d(0.9), 83.038 µm, meaning that 90% of the waste particles are below of this value. These results show that the wastes have fine particles, which can contribute to the ceramic processing.

Table 2: Particle size of the wastes (µm).

<table>
<thead>
<tr>
<th>Wastes</th>
<th>d(0.1)</th>
<th>d(0.5)</th>
<th>d(0.9)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MWE</td>
<td>2.481</td>
<td>16.940</td>
<td>53.762</td>
</tr>
<tr>
<td>MWC</td>
<td>3.126</td>
<td>21.373</td>
<td>77.802</td>
</tr>
<tr>
<td>MBF</td>
<td>2.210</td>
<td>14.884</td>
<td>62.972</td>
</tr>
<tr>
<td>MBE</td>
<td>2.391</td>
<td>17.291</td>
<td>83.038</td>
</tr>
</tbody>
</table>

Fig. 2 shows micrographs of the wastes. A wide particle size range is observed, varying from small to large particles. Most of the particles have an irregular morphology, with angular shape. The MWE waste presents a more homogeneous distribution, confirming the results of particle size in Table 2. The quartz, for having a high resistance to fragmentation and high hardness, can be identified as probably the coarser particles.

Fig. 2: SEM micrographs of wastes. (a) MWE, (b) MWC, (c) MBF, (d) MBE.

The results of the analyzes of the solubilized and leachates extracts of the wastes are observed in Tables 3 and 4. The values of the maximum concentration accepted by the NBR 10004 [4] for both extracts are also shown. The wastes studied presented the results of the elements concentration in the leaching extracts below the limit required by the standard. However, MWE waste presented aluminum (1.22 mg/L) and MBF waste presented total phenols (0.04 mg/L), total aluminum (2.84 mg/L) and total iron (2.25 mg/L) in the solubilized extracts above the limits established by the standard, which are 0.2 mg/L for aluminum, 0.01 mg/L for phenols and 0.3 mg/L for iron [4]. Aluminum can come from the inputs used in the sawing process, from the sawn materials...
themselves and from the water used, which most part is recirculated. The iron probably comes from
the sawing of the blocks due to the use of grit and blade in the cutting. The phenol probably comes
from the resin. According to NBR 10004 [4], the wastes studied can be classified as non inert.

Table 3: Results of the metals/compounds concentration in the solubilization extracts of the wastes
(in mg/L).

<table>
<thead>
<tr>
<th>Elements/compounds</th>
<th>Solubilization extract MWE waste (mg/L)</th>
<th>Solubilization extract MBF waste (mg/L)</th>
<th>Maximum limit NBR 10004 (mg/L) [4]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aluminum</td>
<td>1.22</td>
<td>2.84</td>
<td>0.2</td>
</tr>
<tr>
<td>Arsenic</td>
<td>&lt; 0.001</td>
<td>&lt; 0.001</td>
<td>0.01</td>
</tr>
<tr>
<td>Barium</td>
<td>0.02</td>
<td>0.393</td>
<td>0.7</td>
</tr>
<tr>
<td>Cadmium</td>
<td>&lt; 0.001</td>
<td>&lt; 0.001</td>
<td>0.005</td>
</tr>
<tr>
<td>Chloride</td>
<td>14.0</td>
<td>28.0</td>
<td>250.0</td>
</tr>
<tr>
<td>Copper</td>
<td>0.018</td>
<td>0.007</td>
<td>2.0</td>
</tr>
<tr>
<td>Cyanide</td>
<td>0.005</td>
<td>-</td>
<td>0.07</td>
</tr>
<tr>
<td>Fluoride</td>
<td>0.12</td>
<td>0.54</td>
<td>1.5</td>
</tr>
<tr>
<td>Iron</td>
<td>0.16</td>
<td>2.25</td>
<td>0.3</td>
</tr>
<tr>
<td>Lead</td>
<td>&lt; 0.01</td>
<td>&lt; 0.01</td>
<td>0.01</td>
</tr>
<tr>
<td>Manganese</td>
<td>&lt; 0.01</td>
<td>0.06</td>
<td>0.1</td>
</tr>
<tr>
<td>Mercury</td>
<td>&lt; 0.0001</td>
<td>&lt; 0.0001</td>
<td>0.001</td>
</tr>
<tr>
<td>Nitrate</td>
<td>0.54</td>
<td>-</td>
<td>10.0</td>
</tr>
<tr>
<td>Selenium</td>
<td>&lt; 0.01</td>
<td>&lt; 0.01</td>
<td>0.01</td>
</tr>
<tr>
<td>Silver</td>
<td>&lt; 0.001</td>
<td>&lt; 0.001</td>
<td>0.05</td>
</tr>
<tr>
<td>Sodium</td>
<td>10.7</td>
<td>34.69</td>
<td>200.0</td>
</tr>
<tr>
<td>Sulfate</td>
<td>2.0</td>
<td>-</td>
<td>250.0</td>
</tr>
<tr>
<td>Surfactants</td>
<td>0.13</td>
<td>-</td>
<td>0.5</td>
</tr>
<tr>
<td>Total</td>
<td>&lt; 0.01</td>
<td>&lt; 0.01</td>
<td>0.05</td>
</tr>
<tr>
<td>Chrome</td>
<td></td>
<td>0.04</td>
<td>0.01</td>
</tr>
<tr>
<td>Total Phenols</td>
<td>&lt; 0.003</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Zinc</td>
<td>0.02</td>
<td>0.03</td>
<td>5.0</td>
</tr>
</tbody>
</table>

* - Not determined.

Table 4: Results of the elements concentration in the leaching extracts of the wastes
(in mg/L).

<table>
<thead>
<tr>
<th>Elements</th>
<th>Leaching extract MWE waste (mg/L)</th>
<th>Leaching extract MBF waste (mg/L)</th>
<th>Maximum limit NBR 10004 (mg/L) [4]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Arsenic</td>
<td>&lt; 0.001</td>
<td>0.05</td>
<td>1.0</td>
</tr>
<tr>
<td>Barium</td>
<td>0.07</td>
<td>0.43</td>
<td>70.0</td>
</tr>
<tr>
<td>Cadmium</td>
<td>&lt; 0.001</td>
<td>&lt; 0.001</td>
<td>0.5</td>
</tr>
<tr>
<td>Fluoride</td>
<td>&lt; 0.02</td>
<td>0.82</td>
<td>150.0</td>
</tr>
<tr>
<td>Lead</td>
<td>&lt; 0.01</td>
<td>&lt; 0.01</td>
<td>1.0</td>
</tr>
<tr>
<td>Mercury</td>
<td>&lt; 0.0001</td>
<td>&lt; 0.0001</td>
<td>0.1</td>
</tr>
<tr>
<td>Selenium</td>
<td>&lt; 0.01</td>
<td>&lt; 0.01</td>
<td>1.0</td>
</tr>
<tr>
<td>Silver</td>
<td>&lt; 0.001</td>
<td>&lt; 0.001</td>
<td>5.0</td>
</tr>
<tr>
<td>Total Chrome</td>
<td>&lt; 0.01</td>
<td>&lt; 0.01</td>
<td>5.0</td>
</tr>
</tbody>
</table>

Conclusion

The wastes employed in this investigation are mainly composed of quartz, feldspar phases and
mica. The alkaline oxide content indicates a fluxing potential for ceramic sintering. Particle size
distribution also makes the granite waste a material compatible with ceramics raw materials.
The results of the leaching and solubilization tests showed that both wastes (MWE and MBF) presented limits of the elements/compounds above the allowed by the standard, being classified as non-inert. This result shows that the wastes studied must be applied in materials that can inertize them, as the case with ceramics. A study already carried out by the author shows that the wastes are inertized in the ceramic matrix.

As a final conclusion of this work, it is possible that the studied wastes can be used for their incorporation in clayey mass for the production of ceramics, being a technological and environmental alternative. The use of the waste allows an environmentally correct destination and, therefore, a reduction in the amount of waste to be discarded in the nature. Besides adding value to an undesirable waste, it contributes to the reduction of consumption of natural raw materials, such as clay. Also, it might contribute to the development of a ceramic material with technological properties superior to the material without waste.

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References