Comparative Analysis of Palygorskite Samples From Different Occurrences in Guadalupe (Piauí, Brazil)

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ABSTRACT: Palygorskite is a clay mineral that has several industrial and environmental applications. Palygorskite main deposits in Brazil are located in the municipality of Guadalupe, Piauí. A comparative study was performed with five samples of palygorskite from different locations through ore dressing and chemical and mineralogical characterization, using the XRD, XRF and methylene blue titration techniques. According to the results, there are significant differences in the samples composition. Among them, the most significant difference was the cation exchange capacity (CEC) value, which ranged from 24.0 to 41.0 meq$\cdot$100 g$^{-1}$, followed by the content of some oxides and the crystalline phases present. Despite coming from the same region, the samples contained distinct impurities.

KEYWORDS: Palygorskite; Ore dressing; Characterization.

How to cite

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Received: 27 Nov 2019 | Accepted: 10 Dec 2019

Note: This paper was selected from the 10º Encontro Técnico de Materiais e Química (ETMQ) occurred in 27-29 november of 2019 and organized by Instituto de Pesquisas da Marinha (IPqM) in Rio de Janeiro/RJ, Brazil

Introduction

In Brazil, palygorskite occurrences are limited to the municipality of Guadalupe, Piauí (Baltar et al. 2009) and the Alcântara region in Maranhão (Amorim and Angélica 2011). The Guadalupe region reserves have the highest potential for economic exploitation, especially from Cardoso, Mina Velha, Boa Vista and Angico mines.

Palygorskite is a clay mineral characterized by the unit cell chemical composition of $(\text{Mg,Al})_5\text{Si}_8\text{O}_{20}(\text{OH})_2(\text{OH}_2)_4\cdot4\text{H}_2\text{O}$. Its three-dimensional structure is formed by two sheets of SiO2 tetrahedra with an octahedron formed by Mg$^{2+}$ ions.

Palygorskite fine grain size (< 37 μm) and its fibrous nature associated with ample exchangeable cations give to it a high surface area (125 to 210 m² g$^{-1}$) and a cation exchange capacity (CEC) of 20 to 50 meq 100 g$^{-1}$. Due to these properties, palygorskite has several technological applications, such as in bleaching agents, well-drilling fluids, and adsorbents of toxic metals and pesticides (Luz and Almeida 2005; Murray 2000). Recently, clay minerals such as palygorskite, that contain magnesium, aluminum and silicon in their structure, have been used to prepare cordierite ceramics, which have application in the aerospace area (Thomaidis and Kostakis 2015). For example, because of their high thermal stability, cordierite-family ceramics have been used to manufacture lightweight mirrors for cutting-edge space telescopes (Kamiya and Mizutani 2018).

The aim of this study was to analyze five palygorskite samples in pure fractions from different occurrences located in the region of Guadalupe, Piauí.

Materials and Methods

Four palygorskite samples of approximately 10 kg were collected from Cardoso, Mina Velha, Boa Vista and Angico mines, as well as a sample called GDP that was provided by a local company. The sample collection area is located in the geotectonic context of the Parnaíba Basin in Guadalupe, where the main deposits of palygorskite occur in Brazil. The samples were sent to the Mineral Technology Center (CETEM-MCTIC) to perform the ore dressing and mineralogical characterization steps. To concentrate the clay minerals, the raw samples were dressed by crushing, grinding, wet screening and magnetic separation. Mineralogical characterization of fractions below 20 μm was performed by X-ray diffraction (XRD) and chemical characterization (oxide content) by X-ray fluorescence spectrometry (XRF). The cation exchange capacity (CEC) was determined according to the standard methylene blue titration method based on the American Society for Testing and Materials (ASTM 2019).

Results and Discussion

The XRD results (Fig. 1) indicate that the five samples have a mineralogical composition essentially consisting of palygorskite $(\text{Mg,Al})_5\text{Si}_8\text{O}_{20}(\text{OH})_2(\text{OH}_2)_4\cdot4\text{H}_2\text{O}$, kaolinite $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$ and quartz $\text{SiO}_2$ (Barthelmy 2014). The Angico, Mina Velha and GDP samples showed peaks related to goethite $\text{FeO(OH)}$ (Barthelmy 2014). The Cardoso and Boa Vista samples presented low-intensity peaks attributed to montmorillonite $\text{Na}_{0.2}\text{Ca}_{0.1}\text{Al}_2\text{Si}_4\text{O}_{10}(\text{OH})_2(\text{H}_2\text{O})_10$ and to diaspore $\text{AlO(OH)}$ (Barthelmy 2014), respectively. The Angico sample showed the highest intensity of the clay mineral of interest, with the Cardoso sample presenting the lowest intensity peak. The intensity of the peaks was adjusted according to the second palygorskite peak, at 18.8° (2θ).

The results of the chemical composition to determine oxide content (Table 1) corroborate the results obtained by XRD, since the MgO content in the palygorskite structure was highest for the Angico sample and lowest for the Cardoso sample. Moreover, the higher Al$_2$O$_3$ content of the Cardoso sample may be associated with the presence of montmorillonite. The GDP sample had the lowest SiO$_2$ content, explaining the lower intensity of the quartz peak.
Table 1. Chemical composition of palygorskite samples.

<table>
<thead>
<tr>
<th>Samples (&lt; 20 μm)</th>
<th>Oxis (%) w/w</th>
<th>( \text{SiO}_2 )</th>
<th>( \text{Al}_2\text{O}_3 )</th>
<th>( \text{Fe}_2\text{O}_3 )</th>
<th>( \text{MgO} )</th>
<th>( \text{K}_2\text{O} )</th>
<th>( \text{CaO} )</th>
<th>( \text{TiO}_2 )</th>
<th>( \text{Na}_2\text{O} )</th>
<th>( \text{Loss by calcination} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Boa Vista</td>
<td></td>
<td>53.8</td>
<td>14.2</td>
<td>6.8</td>
<td>5.7</td>
<td>2.2</td>
<td>0.18</td>
<td>0.52</td>
<td>0.14</td>
<td>16.3</td>
</tr>
<tr>
<td>Angico</td>
<td></td>
<td>56.5</td>
<td>12.6</td>
<td>5.5</td>
<td>6.9</td>
<td>1.4</td>
<td>0.21</td>
<td>0.7</td>
<td>&lt; 0.1</td>
<td>15.7</td>
</tr>
<tr>
<td>Cardoso</td>
<td></td>
<td>53.6</td>
<td>16.6</td>
<td>9.2</td>
<td>3.4</td>
<td>1.8</td>
<td>0.17</td>
<td>0.64</td>
<td>0.12</td>
<td>14.4</td>
</tr>
<tr>
<td>GDP</td>
<td></td>
<td>49.5</td>
<td>16.4</td>
<td>7.2</td>
<td>5.4</td>
<td>2.4</td>
<td>0.33</td>
<td>0.60</td>
<td>0.12</td>
<td>18.1</td>
</tr>
<tr>
<td>Mina Velha</td>
<td></td>
<td>53.5</td>
<td>13.5</td>
<td>7.0</td>
<td>5.4</td>
<td>1.9</td>
<td>0.23</td>
<td>0.55</td>
<td>&lt; 0.1</td>
<td>17.8</td>
</tr>
</tbody>
</table>

The CEC values obtained for the Angico, Boa Vista, Cardoso, Mina Velha and GDP samples were 24.0, 24.0, 31.0, 41.0 and 41.0 meq 100g⁻¹, respectively, indicating that all analyzed samples were within the reference values for palygorskite (range of 20 to 50 meq 100g⁻¹) (Murray 2006). The Angico and Boa Vista samples presented the lowest cation exchange capacity, a fact that may be associated with the low \( \text{K}_2\text{O} \) and \( \text{CaO} \) contents of those samples, respectively, since these contents are related to exchangeable cations. In addition, the higher contents of these oxides are associated with higher cation exchange capacity values.

CONCLUSIONS

The palygorskite samples, despite being obtained from the same geological context, contained distinct impurities, such as montmorillonite, goethite and diasporite. Chemical composition corroborated these results. In addition, the samples presented different CEC values, but all values were between 24.0 to 41.0 meq 100g⁻¹. Thus, the results highlight the diversity of applications of this clay mineral, such as adsorbents of herbicides and toxic metals in water bodies and of ammonium in swine wastewater. It is also used in the pharmaceutical industry for controlled drug release and delivery. This clay mineral can be used in other applications, such as oil clarification, soil correction and production of high-strength ceramics, among others.
FUNDING

Fundação Carlos Chagas Filho de Amparo à Pesquisa do Estado do Rio de Janeiro [http://doi.org/10.13039/501100004586]
Conselho Nacional de Desenvolvimento Científico e Tecnológico [http://doi.org/10.13039/501100003593]
Grant 311627/2017-0
Coordenação de Aperfeiçoamento de Pessoal de Nível Superior [http://doi.org/10.13039/501100002322]

AUTHORS’ CONTRIBUTION

Research Idealization, Acquisition of Funding, Samples Collections, Supervision, Bertolino, LC; Conceptualization, Writing - first version, All authors; Characterization and ore dressing of Palygorskite, intellectual and technical support: Simões KMA; Novo BL; Marçano GB; Bertolino, LC; Silva FANG; Teixeira VG; Garrido FMS; Yokoyama L (Cardoso sample); Assis TC; Rodrigues PV; Silva FANG; Pontes FVM; Barbato CN; Teixeira VG; Garrido FMS; Bertolino LC (Mina Velha sample); Cerqueda M; Souza CG; Jesus TC; Spinelli L; Silva FANG; Bertolino, LC (GDP sample); Furlanetto RPP; Silva FANG; Bertolino, LC (Angico sample); Nascimento LCS; Anjos NOA; Silva FANG; Bertolino, LC (Boa Vista sample); Geological support and data interpretation, Campos VMJS; Writing - Review & Editing, Silva FANG, Novo, BL, Barbato CN.

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