Ageing characteristics related to cation exchange and interlayer spacing of some Brazilian bentonites

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1. Introduction

In Brazil, Bentonite, from the commercial point of view (industrial clay), is classified into three main types according to the Brazilian Foundry Association (Associação Brasileira de Fundição) [1]: sodium-raw bentonite, sodium-activated bentonite and calcium bentonite. Sodium-bentonite (Na-montmorillonite) has a high capacity to absorb water, which causes expansion in many times its initial volume, swelling above 30 mL/2 g of clay, and the formation of thixotropic suspensions in water. By contrast, calcium bentonite (Ca-montmorillonite) is characterized by a non-swelling behavior, and therefore, it does not form thixotropic suspensions [2, 3]. Sodium-activated bentonite is a chemically modified bentonite, originally a non-sodium bentonite, whose interlayer cations are replaced by Na+ by means of cation exchanges, usually in soda ash solutions (Na2CO3), a process known as sodium activation [4, 5]. According to the 2015 review of specification E-04 from the Brazilian Commission for the Study of Raw Materials (Comissão de Estudos de Matérias Primas – CEMP) [1], sodium-activated bentonite is classified into three types based on swelling: Type I (≥35 mL/2 g), Type II (≥30 mL/2 g) and Type III (≥26 mL/2 g).

From the point of view of academic research, bentonite is classified into at least five types: sodium, calcium, magnesium, potassium and mixed-cationic or polycationic, given the numerous studies on the subject [6, 7, 8, 9]. Many of the bentonites classified as calcium based only on swelling are actually magnesium or mixed-cationic, which also do not swell, and this has led to the misclassification of some bentonites that do not swell as calcium bentonites [5]. The same applies to the mineralogical characterization and total chemical analysis [10].

Depending on the cationic characteristics, bentonites are used for different purposes. For example, calcium bentonites are used in the clarification of oils and drinks, whereas sodium bentonites are used as pet litter, oil and water well drilling fluids, and foundry molds and in iron ore pelletization [3]. Non-sodium bentonites are more abundant than sodium bentonites [2], which are not known to occur in Brazil [4].

According to the Brazilian National Department of Mineral Production (Departamento Nacional de Produção Mineral) [11], of the total bentonite imports in 2014, approximately 94% were sodium-raw bentonite, and the remaining ~6% were sodium-activated bentonite. In that same year, 70.2% of the national consumption of sodium-activated bentonite was for iron ore pelletization and for foundry molds. These numbers demonstrate the importance of this commodity for the large national industry.

Some Brazilian bentonite miners have reported losses of the specified rheological and functional properties of their products (sodium-activated bentonites) due to the ageing of their products. This study investigated the influence of cation type on the sodium deactivation of Brazilian bentonite varieties. Four bentonite clays were studied, including three mixed-cationic and one magnesium. Swelling and the main exchangeable cations (Na+, K+, Mg2+ and Ca2+) were the main evaluation parameters in this study. Periodic washes of the sodium-activated bentonites were performed based on the hypothesis that a possible desorption of the cations (primarily Na+) could cause the deactivation. Sodium activation was monitored using XRD measurements and an increase in swelling. Sodium deactivation was observed and monitored via a decrease in swelling. Positive and negative effects, caused by the proportions of the cations and the dominance of Mg2+, were emphasized by the set of cationically different samples applied in this study, which helped to answer the influence of main exchangeable cations, specially Mg2+, on the deactivation process.

ARTICLE INFO

Keywords:
Bentonite
Sodium deactivation
Cation type
Exchangeable cations

ABSTRACT

This study investigated the influence of cation type on the sodium deactivation of Brazilian bentonite varieties. Four bentonite clays were studied, including three mixed-cationic and one magnesium. Swelling and the main exchangeable cations (Na+, K+, Mg2+ and Ca2+) were the main evaluation parameters in this study. Periodic washes of the sodium-activated bentonites were performed based on the hypothesis that a possible desorption of the cations (primarily Na+) could cause the deactivation. Sodium activation was monitored using XRD measurements and an increase in swelling. Sodium deactivation was observed and monitored via a decrease in swelling. Positive and negative effects, caused by the proportions of the cations and the dominance of Mg2+, were emphasized by the set of cationically different samples applied in this study, which helped to answer the influence of main exchangeable cations, specially Mg2+, on the deactivation process.

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https://doi.org/10.1016/j.heliyon.2021.e06192
Received 13 May 2019; Received in revised form 24 January 2020; Accepted 1 February 2021
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90% of the Brazilian bentonite production [16, 17]. The well-known Boa Vista region (Paraíba state), responsible for more than
There are discussions in the literature about the factors that influence the sodium activation process and about the effect of this process on the properties of the activated bentonite, such as the activation mechanism (cation exchange diffusion), ageing time, initial moisture content of the bentonite, Na₂CO₃ dosage, viscosity of the thixotropic pulp of the bentonite in water (apparent and plastic viscosities), impermeability, thermal stability and binding strength [7, 13, 14, 15]. However, in general, little has been discussed or investigated regarding the small, medium and high grade polycationic or mixed-cationic (these terms will be used in the present study) of Brazilian bentonites, an aspect that may greatly influence the sodium deactivation. In this context, we sought to investigate the influence of the cation type of four well-characterized Brazilian bentonites on their sodium deactivation.

2. Materials and methods

2.1. Raw bentonites

Four Brazilian bentonites were considered in this study, mainly based on their place of origin, color and cation type: Chocolate, Verde Lodo, Bofe and Formosa (Table 1). The first three bentonites come from the well-known Boa Vista region (Paráiba state), responsible for more than 90% of the Brazilian bentonite production [16, 17].

| Bentonite   | Color  | Place of origin           | Exchangeable cation type          |
|-------------|--------|---------------------------|----------------------------------|
| Chocolate   | Brown  | Boa Vista, Paraíba State  | Polycationic or mixed [16, 17]   |
| Verde Lodo  | Green  |                           |                                  |
| Bofe        | Beige  |                           |                                  |
| Formosa     | Red    | Formosa da Serra, Negra, Maranhão State | Magnesium [5, 18] |

Table 1. Four Brazilian bentonites used in this work.

The scientific cationic classification is adopted here (based on five types) rather than the commercial classification (based on only three types) and is presented and discussed in the Introduction. The bentonites deposits are well known and have been exploited for a long time (since the 1960s), with the exception of Formosa bentonite. The economic potential and, especially, the interest in studying Formosa bentonite lies in its cation type (Mg²⁺), which is scarcely described in the literature [5, 8, 10].

2.2. Sodium activation

First, the clays were dried at 60 °C in an oven, fragmented in a jaw crusher (model BB2, Retech) and homogenized and quartered by the conical quartering method. A quantity of 600 g of each clay was mixed with 223 mL of Na₂CO₃ (887 mmol.L⁻¹). This sodium activation ratio corresponds to 3.5% Na₂CO₃/dry clay (m/m) and 22% moisture. The activation procedure consisted of wetting the clay with the sodium solution by dripping and manual mixing. After an ageing time of 24 h, the samples were dried at 60 °C and crushed in a shaker box (model 8515-115, SPEX Sample Prep). The activated samples were identified by adding the suffix ‘Act’, as follow: Chocolate-Act, Verde Lodo-Act, Bofe-Act and Formosa-Act.

2.3. Washing

In traditional industrial sodium activation, there is no washing step. Therefore, in this study, we sought to investigate this variable based on

the hypothesis that sodium deactivation is caused by cation exchange, considering activation a reversible process [12], because all cations remain in the clay system. Thus, 10 g of each activated clay was mixed with 0.25 L of deionized water and left to rest for 24 h. The supernatant was centrifuged at 4500 rpm for 10 min to recover the fine fraction, which was added to the decanted coarse fraction, dried at 60 °C and crushed in an agate mortar. The washed samples were identified by the suffix ‘Wsh’, as follow: Chocolate-Wsh, Verde Lodo-Wsh, Bofe-Wsh and Formosa-Wsh.

2.4. Sodium deactivation

The deactivation was studied through the swelling capacity test, which is a low cost analysis that provides quick answers and preliminary information on the properties and rheological behavior of bentonite. According to Silva et al. (2017) [12], the reversibility of activation reactions can be indirectly verified by rheological control. This test was performed according to the recommended Brazilian standard CEMP 058 [18] by adding 2 g of dry clay to 100 mL of distilled water in a graduated cylinder. This analysis was performed in the following time steps: 1) raw clays: only once; 2) activated clays: twice a week during 95 days; and 3) washed clays: once a week during 109 days.

2.5. Analyses

X-ray diffraction (XRD) was performed on an XPERT PRO MPD X-ray diffractometer (PANalytical) equipped with a 0-0 goniometer and a model PW3373/00 ceramic X-ray tube with a Cu anode (Kα1 = 1.540598 Å), a fine focus (2200 W/60 kV), and a Kβ nickel filter. An X'Celerator RTMS detector was used. The analysis conditions were as follow: scanning from 3 to 74°2θ, 40 kV, 30 mA, a step size of 0.02°2θ, a time/step of 20 s, a 1/2° fixed slit and 1° antiscattering, a 10 mm mask, and 1 rps spinning. The software used to interpretation was HighScore Plus (PANalytical).

Chemical analysis was performed using inductively coupled plasma-optical emission spectrometry (ICP-OES) in a Vision ICP at the Acme Analytical Laboratories Ltda. in Vancouver, Canada. For this analysis, the clays were mixed with lithium metaborate and tetraborate, melted in an oven and dissolved in nitric acid. The loss on ignition (LOI) analysis was performed in a muffle furnace at 1000 °C for 1 h. The Na⁺, K⁺, Mg²⁺ and Ca²⁺ exchangeable cation contents of the raw bentonites were obtained by the Brazilian Agricultural Research Corporation (Empresa Brasileira de Pesquisa Agropecuária – EMBRAPA) according to the procedure described in the Manual of Chemical Analysis Methods for Soil Fertility Assessment [19]. Na⁺ and K⁺ were extracted with Mehlich’s solution and obtained in a flame photometer (model BFC 150, Benfer); Mg²⁺ and Ca²⁺ were simultaneously obtained by extraction with 1 M KCl and complexometric titration with EDTA (disodium salt) and eriochrome T black as the indicator; then, Ca²⁺ was obtained via complexometry with EDTA, using calciocarbonic acid as the indicator; and the Mg²⁺ value was calculated by difference.

The moisture content was measured by heating 1 g of each raw and activated sample at 60 °C for 24 h. This procedure was performed prior to the swelling test. For raw and activated clays, the moisture water adsorption capacity as a function of the exchangeable cations was also evaluated.
3. Results and discussion

3.1. Mineralogical and chemical compositions and exchangeable cations

The montmorillonite-type smectite is the predominant clay mineral in all bentonites (Figure 1). It is characterized by its main 001 reflection between 14.4 and 15.6 Å [20], as predicted in the study by Paz et al. (2012) [5], who characterized these samples in detail. Other important reflections in the characterization of smectites are: d100 – 4.46 Å and d060 – 1.49 Å, the latter a characteristic of dioctahedral smectites, with the montmorillonite species being the most abundant and characteristic of bentonites [5, 21]. Accessory minerals such as anatase (3.52 Å) were found in all samples, as well as quartz (3.34 and 4.25 Å), goethite (4.17 Å), and hematite (2.69 Å) in Chocolate bentonite; illite (9.95 Å), kaolinite (7.20, 3.57 and 2.56 Å), quartz (3.34 and 4.25 Å) and K-feldspar (3.24 and 4.22 Å) in Verde Lodo bentonite; kaolinite (7.21 and 2.56 Å), quartz (3.34 Å), hematite (2.70 Å) and cristobalite (4.09 and 2.50 Å) in Bofe bentonite; and kaolinite (7.23 Å), hematite (2.70 and 2.51 Å) and K-feldspar (4.24, 3.78, 3.32 and 3.24 Å) in Formosa bentonite.

The chemical composition of the bentonites are shown in Table 2. The SiO₂ content is predominant in all samples, being highest in the bentonite Bofe (62.3%) and lowest in Formosa (45.1%). The differences in SiO₂ content may be explained by the different contents of accessory silicates. Silicon is one of the basic elements in the formation of montmorillonite (tetrahedral sheets), and therefore, one might expect its predominance; it is also present in illite, kaolinite, quartz, K-feldspar and cristobalite. Aluminum is the second most abundant element in the samples, varying from 12.5% in the Bofe bentonite to 20.3% in Verde Lodo; this element is present in the structure of montmorillonite (octahedral sheet), illite, kaolinite and K-feldspar.

The iron content ranges from 7.1% in Bofe bentonite to 13.9% in Formosa bentonite. Iron is associated with isomorphic substitutions in the octahedral sheets and interlayer space of montmorillonite and with the accessory iron minerals goethite (Chocolate and Verde Lodo) and hematite (Bofe and Formosa). The magnesium content ranges from 1.9% in Bofe bentonite to 3.8% in Formosa bentonite; similar to iron, it may also be associated with isomorphic substitutions in the octahedral sheets and interlayer space of montmorillonite. Potassium varies from 0.2% in Bofe bentonite to 1.7% in Formosa bentonite; in addition to being present in the interlayer space, this element is also found in illite and in K-feldspar, thus explaining its high content in the Verde Lodo (1.4%) and Formosa (1.7%) bentonites.

Calcium and sodium are exclusively associated with the interlayer space of montmorillonite; their contents range from 0.2% (Bofe) to 0.9% (Chocolate) and from 0.02% (Formosa) to 0.6% (Bofe), respectively. Titanium ranges from 0.61% to 1.44% and is related to anatase, present in all samples. The other quantified elements are below 0.15%. The LOI contents range from 14.4% in Bofe bentonite to 18.3% in Chocolate bentonite.

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| Table 2. Chemical composition of in natura bentonites. |
|-----------------------------------------------|
| Constituent | % Mass | Chocolate | Verde Lodo | Bofe | Formosa |
| SiO₂ | 51.3 ± 0.4 | 47.4 ± 0.3 | 62.3 ± 0.7 | 45.1 ± 0.1 |
| TiO₂ | 0.85 ± 0.01 | 1.29 ± 0.01 | 0.61 ± 0.01 | 1.44 ± 0.01 |
| Al₂O₃ | 16.2 ± 0.05 | 20.3 ± 0.10 | 12.5 ± 0.03 | 16.9 ± 0.04 |
| Fe₂O₃ | 7.7 ± 0.2 | 10.5 ± 0.3 | 7.1 ± 0.1 | 13.9 ± 0.1 |
| CaO | 0.9 ± 0.005 | 0.4 ± 0.010 | 0.2 ± 0.000 | 0.3 ± 0.005 |
| MgO | 3.4 ± 0.005 | 2.2 ± 0.010 | 1.9 ± 0.005 | 3.8 ± 0.030 |
| MnO | 0.01 ± 0.000 | 0.11 ± 0.000 | - | 0.13 ± 0.010 |
| K₂O | 0.6 ± 0.000 | 1.4 ± 0.005 | 0.2 ± 0.005 | 1.7 ± 0.015 |
| Na₂O | 0.5 ± 0.005 | 0.5 ± 0.005 | 0.6 ± 0.010 | 0.02 ± 0.000 |
| P₂O₅ | 0.03 ± 0.010 | 0.10 ± 0.000 | 0.06 ± 0.010 | 0.10 ± 0.000 |
| LOI | 18.3 ± 0.3 | 15.5 ± 0.1 | 14.4 ± 0.7 | 16.4 ± 0.1 |
| Total | 99.8 | 99.7 | 99.9 | 99.8 |
| LOI: Loss on ignition; and (-): Below detection limit. |

| Table 3. Exchangeable cation contents of in natura bentonites. |
|-----------------------------------------------|
| Bentonite | EC (mg/dm³) | Na⁺ | K⁺ | Mg²⁺ | Ca²⁺ |
| Chocolate | 1171 | 186 | 4838 | 6493 |
| Verde Lodo | 1149 | 186 | 3829 | 2605 |
| Bofe | 910 | 29 | 2601 | 1002 |
| Formosa | 65 | 79 | 5761 | 1723 |
The main exchangeable cation contents, Na\(^+\), K\(^+\), Mg\(^{2+}\) and Ca\(^{2+}\) (related to montmorillonite of the studied bentonites), are presented in Table 3, in mg/dm\(^3\). As a way to better visualize the predominance of cations, those values were normalized to 100% and presented in Figure 2. The Na\(^+\) content is higher in Bofe (20.0%) and lower in Formosa (0.9%). Comparison of all the bentonites reveals a trend toward increasing Mg\(^{2+}\) content from Chocolate to Formosa bentonite (38.1%–75.5%, respectively), with decreasing Ca\(^{2+}\) content (51.2%–22.6%, respectively), suggesting a competition between bivalent cations. In addition, these data are in agreement with the mixed-cationic \cite{16} and magnesian \cite{5, 10} nature of bentonites.

Notably, in the cation distribution of each sample, the Formosa bentonite concentrates bivalent cations, especially Mg\(^{2+}\), and has no content higher than 1% in the other cations, whereas in the other bentonites, in addition to the Mg\(^{2+}\) and Ca\(^{2+}\) contents, Na\(^+\) content is higher. Thus, the present study suggests a classification based on the cation type, in which Formosa is designated homionic, whereas Bofe, Verde Lodo and Chocolate are heterionic of high, medium and low grade for Mg\(^{2+}\), respectively, and similarly for Na\(^+\).

3.2. Sodium activation and changes in basal spacing, moisture and swelling

After sodium activation, the 001 reflection decreased from \(~15\ \text{Å}\) to \(~12\ \text{Å}\) (Figure 3), which confirms the majority entry of Na\(^+\) into the interlayer space of the smectites, transforming them into sodium-activated bentonites \cite{22}.

The moisture content of the clays before and after activation reveals the change in moisture adsorption capacity after this treatment and in the 001 reflection. The content of all bentonites, initially non-sodium bentonites, decreased with sodium activation, that is, sodium has a lower capacity for moisture water adsorption and for hydration water adsorption (also known as water of constitution or structural water). The dimension of the interlayer space of a smectite depends on the cations that occupy it because they hydrate \cite{14}; as the hydration capacity of alkaline earth metals is higher than that of the corresponding alkali metals because their hydration energies are higher due to the lower ionic radius and higher charge \cite{23}, there is a decrease in basal spacing. Thus, there are two types of swelling: 1) intracrystallite swelling: acts at smaller distances due to the hydration of the exchangeable cations, resulting in a distancing/approximation of the layers \cite{24} (Figures 3 and 4), for example, sodium activation; and 2) osmotic swelling: acts at higher distances due to the water entrance (beyond intracrystallite swelling) between the layers. This entrance aims the osmotic balance between the concentration of exchangeable cations and the pore water, resulting in their distancing \cite{22, 24}, for example, swelling behavior.

As an additional consequence of sodium activation, the swelling values of the raw and activated bentonites were changed (Table 4). Prior to activation, the swelling values of the bentonites from the state of Paraíba, characterized as calcium bentonites \cite{1}, are quite close to each other, varying from 11.0 mL in the Verde Lodo bentonite to 13.0 mL in the Chocolate bentonite. These values are high compared to that of Formosa bentonite (4.5 mL), characterized as a magnesia bentonite. Routinely, the swelling of bentonites is attributed only to exchangeable Na\(^+\) because its hydration (osmotic swelling) is significantly different from those of Mg\(^{2+}\) and Ca\(^{2+}\) \cite{25}; however, one should also consider the influence of these two cations (especially Mg\(^{2+}\)) because the swelling of the Chocolate bentonite showed the highest value (13.0 mL), as it contains the lowest Mg\(^{2+}\) content, 38.1% (and 9.2% Na\(^+\)) (Figure 2). In contrast, Formosa reached the lowest swelling, containing 75.5% Mg\(^{2+}\) (and 0.9% Na\(^+\)) (Figure 2).
Although Bofe had the second highest Mg\(^{2+}\) content (57.3%) among all bentonites, its swelling (12 mL) exceeded the swelling of Verde Lodo (11.0 mL), which contained 49.3% Mg\(^{2+}\), which can be attributed to the higher Na\(^+\) content (20.0%) in Bofe. These behaviors confirm that the influence of cation type on the swelling of bentonites is primarily a function of these two interlayer cations, Na\(^+\) and Mg\(^{2+}\). Notably, from the industrial point of view, there is no interest in knowing which cations are present in the interlayer space of a smectite, provided that it presents the desired thixotropic properties (naturally or after activation). However, bentonites may exhibit different behavior as a function of cationic diversity (Figure 2 and Table 4), even those from the same locality because the proportion of exchangeable cations can vary radically in small extensions up to a few centimeters within a single deposit [26].

After sodium activation, there was a significant increase in the swelling value, ranging from 20.0 mL in the Formosa-Act bentonite to 43.5 mL in the Chocolate-Act bentonite. This behavior corroborates the cation exchange of mixed-cations for Na\(^+\), producing good swelling and viscous suspensions [4, 24, 27]. In practice, when in contact with water, calcium smectites (which predominantly contain Mg\(^{2+}\) and Ca\(^{2+}\)) tend to flocculate instead of swell, due to the strong bond that these cations promote between the layers. Conversely, a weak bond between the monovalent cations (Li\(^+\) and Na\(^+\)) and the layers favors the excessive intake of water molecules (swelling) [22, 24, 25, 28, 29, 30]. K\(^+\) is an exception because it has greater difficulty hydrating due to its greater ionic radius [28].

### 3.3. Monitoring the deactivation and behavior of washed bentonites

Chocolate-Act showed a swelling of 43.5 mL shortly after sodium treatment (Figure 5A). However, this result had a marked decrease immediately after sodium activation, followed by a milder decrease and stabilization at 35.5 mL starting on day 50. Chocolate-Wsh initially showed a considerable decrease from 43.5 mL to 35.5 mL; the value then increased, reaching 40.5 mL close to the 30th day, and decreased again, reaching a minimum of 32.5 mL (Figure 5A).

With the activation, Verde Lodo-Act showed a swelling of 33.3 mL, followed by a marked decrease and stabilization at ~26 mL starting on day 42 (Figure 5B). Verde Lodo-Wsh showed a significant decrease in swelling on the days following activation, from 33.3 mL to 20 mL. Subsequently, the value increased to a maximum of 23.5 mL between the 31st and 47th days, followed by a gradual decrease, reaching a minimum value close to 21 mL (Figure 5B).

Bofe-Act showed no decrease in the swelling value after sodium activation; this was the only sample that showed little variation and remained stable over time, with swelling near 22 mL (Figure 5C). The results for Bofe-Wsh were initially very stable, close to 22 mL, followed by an improvement, reaching 25 mL close to the 40th day; on subsequent days, despite oscillating and decreasing in value, the swelling value remained close to the maximum value (24 mL).

Similar to the behavior of Chocolate-Act and Verde Lodo-Act, Formosa-Act initially showed a marked decrease in swelling, from 20 to 17 mL, followed by a smoother decrease and stabilization close to 15 mL (Figure 5D). Formosa-Wsh, which started with a swelling value of 20 mL and decreased to 13 mL, then reached an increase to a maximum of 16 mL near the 30th day and a subsequent decrease to a minimum of 13.5 mL (Figure 5D).

Among the activated bentonites, Chocolate-Act and Verde Lodo-Act reached swelling values corresponding to the Type I (≥35 mL) and Type II (≥30 mL) specification [1], respectively. In general, Chocolate-Act was above this value throughout the study period, which may indicate that the cation exchange produced by the sodium activation occurred more efficiently with this bentonite, suppressing the influence of Mg\(^{2+}\). Similarly, Verde Lodo-Act presented stabilization, however, close to 26 mL, which would specify it as an Activated Type III bentonite [1]. On the other hand, Bofe-Act and Formosa-Act, although presenting swelling, obtained values corresponding to the specification of calcium bentonite (<26 mL) [1].

The optimal swelling results for the Chocolate and Verde Lodo bentonites (especially Chocolate) may be due to the fact that they show the lowest contents of Mg\(^{2+}\) (low and medium grade mixed-cationic for

| Table 4. Swelling of the in natura and activated bentonites. |
|----------------------------------|------------------|
| Bentonite | In natura | Activated |
|-----------|-----------|-----------|
| Chocolate | 13.0      | 43.5      |
| Verde Lodo| 11.0      | 33.3      |
| Bofe      | 12.0      | 22.0      |
| Formosa   | 4.5       | 20.0      |

Figure 5. Swelling behavior of the activated and washed bentonites over time: A) Chocolate; B) Verde Lodo; C) Bofe; and D) Formosa.
Mg\(^{2+}\), respectively; Figure 2) and, with sodium activation, these contents decreased. On the other hand, the cation exchange may not have been sufficient to overcome the influence of Mg\(^{2+}\) on the Bofe and Formosa bentonites. This shows that the swelling reflects the influence of the predominant cation type and its degree of distribution (proportion). The Chocolate bentonite (low grade mixed-cationic for Mg\(^{2+}\)) provides the best thixotropic results, and therefore, industrially, this bentonite is blended with others with different characteristics and with various rheological behavior.

Because Bofe-Wsh reached higher swelling values than the initial sample, at the end of the study period, among the washed bentonites, this indicates that for this cation type (high grade mixed-cationic for Na\(^{+}\)), the washing was more efficient.

### 3.4. Swelling and exchangeable cations after washing

The decreasing Na\(^{+}\) content and increasing Mg\(^{2+}\) content in the first 14 days favored the decreased swelling of the Chocolate-Wsh bentonite (Figure 6A). This decrease is directly related to the influence of these two exchangeable cations, as already discussed. The swelling of this bentonite increased, followed by a subsequent decrease, suggesting that Na\(^{+}\) adsorption and Ca\(^{2+}\) desorption occurred, followed by adsorption of Ca\(^{2+}\) and desorption of Na\(^{+}\). However, the swelling values of this bentonite maintained its specification as Type II (≥30 mL/2 g) [1].

The Verde Lodo-Wsh bentonite reached the highest decrease in Na\(^{+}\) content (5%) among all bentonites and, as expected in support of our hypothesis, presented the highest increase in Mg\(^{2+}\) content. This helps to explain why the Verde Lodo-Wsh bentonite showed the largest decrease in swelling (13 mL) in the initial 14 days (Figure 6B). The subsequent improvement of these results was not significant, and the calcium bentonite specification (<26 mL) was maintained [1].

The swelling of Bofe-Wsh did not change in the first 14 days, which is precisely expected for the bentonite with the highest Na\(^{+}\) grade (Figure 6C). This may explain why its swelling value remained above the initial value; nevertheless, it remained within the calcium bentonite specification (<26 mL) [1], probably because of the high Mg\(^{2+}\) grade.

The Mg\(^{2+}\) content in Formosa-Wsh bentonite was slightly changed even after the sodium activation, revealing its high attraction for the interlayer space (Figure 6D). This was also the bentonite that presented the smallest swelling value. The increase in the swelling value observed after the initial 14 days was due to Na\(^{+}\), but it was not sufficient to bring this bentonite to the level of type I, II or III. The specification of this bentonite remained as a calcium bentonite (<26 mL) [1].

After the initial 14 days, the changes in the cations contents were quite subtle but may have strongly influenced the variations in swelling values. This subtlety demonstrates the strong effect of these cations on this property. The Bofe-Wsh was the only bentonite that had its cation contents mostly concentrated in Na\(^{+}\) and Mg\(^{2+}\), and Formosa-Wsh was concentrated in Mg\(^{2+}\). Finally, Mg\(^{2+}\) is the cation that most negatively affects swelling.

### 4. Conclusions

Sodium deactivation of four Brazilian bentonite varieties was studied based on the premise that the cation type exerts a strong influence on this process. With great clarity, the results confirmed this premise through the positive and negative effects (swelling) caused by the proportions of the cations and by the dominance of one of them.

The set of cationically different samples applied in this study helped us to answer some of our questions as to what causes or accelerates deactivation. From the obtained results, it was possible to conclude that the Mg\(^{2+}\) interlayer exerts the greatest influence on the sodium activation process and on sodium deactivation. Due to its strong attraction for the interlayer space, the greater the amount of Mg\(^{2+}\) in the cation exchange medium, the greater its presence will be in the interlayer space of montmorillonite.

### Declarations

**Author contribution statement**

A.L.V. Carmo: Conceived and designed the experiments; Performed the experiments; Analyzed and interpreted the data; Contributed reagents, materials, analysis tools or data; Wrote the paper.

R.S. Angélica: Analyzed and interpreted the data; Contributed reagents, materials, analysis tools or data; Wrote the paper.

S.P.A. Paz: Conceived and designed the experiments; Analyzed and interpreted the data; Contributed reagents, materials, analysis tools or data; Wrote the paper.
Funding statement

This work was supported by the Brazilian agency: CAPES (Higher Education Personnel Improvement Coordination) who awarded an MSc scholarship to the first author, A.L.V. Carmo, and a grant to the second author, R.S. Angélica (305.392/2014-0).

Data availability statement

Data included in article.

Declaration of interests statement

The authors declare no conflict of interest.

Additional information

No additional information is available for this paper.

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