Purification of Bentonite clays from Cubati, PB, Brazil, for Diversified Applications

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Abstract. The State of Paraíba, Brazil, retains about 88.5% of all Brazilian bentonite, and much of this production comes from deposits in the District of Boa Vista, PB. Nevertheless, the deposits are almost depleted. Recently, new deposits were found, which will increases the reserves of the State, in the regions of Cubati and Pedra Lavrada, PB. The objective of this work is to characterize and develop purified clays, through sieving and hydrocycloning techniques, from those recently discovered bentonites for several applications. The characterization of the sample was done through granulometric analysis by laser diffraction, X-ray diffraction, chemical analysis by X-ray fluorescence, and thermogravimetric and differential thermal analysis. The results show that the samples are typical of bentonite clays, and that the purification solely by hydrocyclone presents the best results.

Introduction

According to Souza Santos [(1)], smectite clays are materials constituted by one or more smectitic clay minerals and by some accessory minerals, mainly quartz, cristobalite, mica and feldspars, being usually referred to as bentonites.

Bentonite clays are constituted by lamellae formed by a octahedral leaf of aluminum hydroxide ($Al_2(OH)_6$) between two tetrahedral leafs of silica (SiO_2); in the octahedral positions the cations can be Al^{3+}, Mg^{2+}, Fe^{3+}, and in the tetrahedral layer we may have isomorphic exchanges Si^{4+} by Al^{3+}. Regardless of the cations, the layers will be electrically unbalanced, with an approximate deficiency of 0.66 of positive charge per unitary cell. This deficiency is balanced mainly by hydrated cations reversibly fixed to the layers, thus being replaceable by other cations [(1,2)].

Bentonite clays are widely used in many sectors of industry, being used in the production of organoclays for incorporation in organic matrices for obtainment of polymeric nanocomposites, as well as in charges of polymers and elastomers, inks, varnishes, pharmaceutical industry, sand binder in casting molds, in the discoloring of oils, desiccants, waterproofing of dams, and in drilling fluids and muds [(3,4)].

The sieving technique is intended to separate the granular material into two or more different classes of particle sizes, through one or more surface with holes with defined dimensions. The usual objectives of sieving are: avoiding the entrance of smaller particles downstream, or undersize in the device; avoiding the oversized particles pass to the next stages; gauge the material properly to increase the efficiency of the downstream operations (formation of pauci-disperse flow) or to adapt a product to certain specifications, or even to purify the clays in industrial scale, avoiding the passage of accessory minerals [(5)].

Hydrocyclone, on the other hand, are devices that make the solid-liquid separation and can be a very efficient and affordable tool for purifying natural clays in industrial scale, separating the grosser fractions, due to the presence of accessory minerals, from the finer fractions, which consist of the clay mineral. The hydrocyclone is constituted of a conic part connected to a cylindrical one, where there is a tangential inlet for the feeding suspension. The upper part of the hydrocyclone has a tube to output the diluted suspension (overflow) and in the bottom there is the output hole for the concentrated suspension (underflow). The separation principle of hydrocyclones is provided by the centrifuge sedimentation, through which the particles in suspension are subjected to a centrifuge field which causes the separation of the fluid (6).

The main bentonite fields in operation in Brazil are located in the District of Boa vista, in the State of Paraíba. The disordered exploration of those fields for many years is now causing their depletion, which will result in a serious problem for the national petroleum production (7, 8, 9).

The purpose of this work is the characterization and development of purified clays applying sieving and hydrocycloning techniques to the bentonites recently discovered in the District of Cubati, PB, for use in many industrial applications.

Materials and Methods

Materials. We used a polycationic Superior Gray type bentonite from mines in Campos Novos Farm, in the District of Cubati, PB.

Methods. The methodology basically consists in the definition of the most efficient procedure for purifying the clays (either in sieves, or by hydrocycloning, or both), which was evaluated through the characterization of the samples.

Purification by sieving. We gathered a representative clay sample (200g) which was put in a stove in a temperature of 60 ± 5^{o}C, for 48h. We added 1000ml of distillated water to 100g of dry clay. The mixture of clay and water was done with help of a Hamilton Beach agitator at low rotation (1800 rpm) for a period of 7 days, having the suspension agitated for six hours per day. After that period, with the hydrated sample, the material was slightly agitated and sequentially transferred to a set of ABNT sieves, n^o. 35 (0.500 mm), n^o. 100 (0.149 mm), n^o. 200 (0.074 mm) and n^o. 325 (0.044 mm). So, the material passing through each sieve passed to the next one, with smaller hole dimensions, and we kept only the material which passed the ABNT n^o. 325 (0.044 mm) sieve.

Purification by hydrocycloning. The dry clay sample was dispersed in a concentration of 4% in mass, in a volume of 30L and kept under agitation for a period of 24 hours at room temperature. After that period, the dispersion was pumped, with help of a centrifuge pump, to the hydrocyclone with pressure varying from 3 to 3.5bar. There, the flow was separated into "overflow" and "underflow". The underflow is gathered in the lower part, apex (tailing) and the overflow in the upper part, vortex (purified). The holes used, the vortex and the apex, can vary, and this variation results in the modification of concentration and of the flow. A combination of the dimensions of the inner diameters of vortex and apex originate six distinct configurations (A1, A2, A3, B1, B2, B3). To determine which configuration is the most efficient in the purification, this process was developed in the six combinations and the analysis of this efficiency was carried out with help of characterization techniques.

Characterization techniques. The characterization of the sample of the studied clay was done by means of the following techniques: granulometric analysis by laser diffraction (GA), chemical analysis by X-ray fluorescence (EDX), X-ray diffraction (XRD), thermogravimetric analysis (TGA) and differential thermal analysis (DTA), following the indications in Ferreira (10). The samples processed by hydrocycloning were characterized through GA and XRD.

Results and Discussion

Characterization of natural samples

Table 1 presents the result of the granulometric analysis by laser diffraction, with respect to the clay, silt and sand content of the studied clay, after passing through an ABNT sieve nº. 200 (0.074mm) and dispersed in water. Notice that the clay presented a large and monomodal particles distribution curve, tending to bimodal, were we can observe a concentration of particles sizes between 4 and 9μm, being obtained a mean particles diameter of 9.19μm. It is also possible to notice a percentage of accumulated volume with diameter below 2.0μm, equivalent to 11.96%, corresponding to the clay content. The accumulated volume of silt (particle diameter above 2μm and below 20μm) was 76.53%. Comparing the results of particles size distribution determined by FERREIRA [13] for the Chocolate bentonite from Boa Vista, PB, and the Superior Gray clay, we notice similar results, which suggests that this sample has similar physical characteristics to the smectites from Boa Vista, PB.

Table 1. Granulometric distribution per particle size of the clay from Cubati, PB

Sample	*Clay (%) ($x<2\mu m$)*	*Silt (%) ($2\mu m<x<20\mu m$)*	*Sand (%) ($x>20\mu m$)*	*Mean diameter (μm)*
Superior Gray	11.96	76.53	11.51	9.19

Table 2 presents the chemical analysis by X-ray fluorescence of the Superior Gray clay sample from Cubati, PB. Analyzing these results, we observe that this clay has typical chemical composition of bentonite clays [1, 7,11].

Table 2. Chemical composition of the clays from Cubati, PB.

Sample	*Oxides (%)*								
	SiO_2	*Al_2O_3*	*Fe_2O_3*	*CaO*	*MgO*	*Na_2O*	*Ti_2O*	*Other*	*LOI*
Superior Gray	55.0	30.0	3.2	0.5	2.2	0.5	1.0	1.257	7.3

LOI – Loss on Ignition.

Figure 1 presents the X-ray diffraction of the Superior Gray clay. Analyzing Figure 1, we observe the presence of the following mineralogical phases: smectite, characterized by 15.77Å and 2.55Å; kaolinite, characterized by the interplanar distances of 7.14Å, 4.45Å and 3.57Å and quartz, characterized by 3.32Å, 3.15Å and 1.67Å. We notice that this clay has a typical bentonite diffractogram [1,7,11]. The presence of the smectite peak was confirmed by the used of ethylene glycol with the expansion of the interplanar basal distance to 17.0 Å [1].

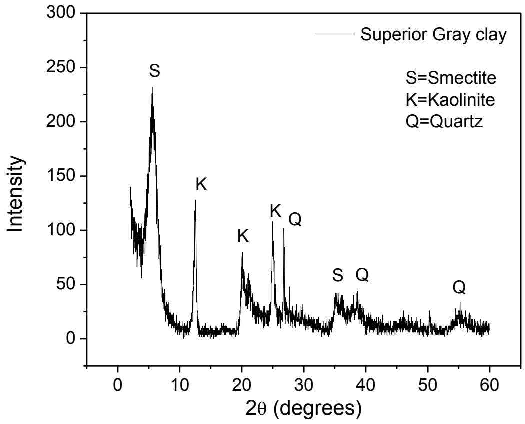

Figure 1. XRD of the Superior Gray clay.

Figure 2 presents the thermal differential and thermogravimetric analyses of the Superior Gray bentonite. Analyzing Figure 2, we observe the following thermal transformations: endothermic peak around 138ºC, characterizing the presence of free and adsorbed water; endothermic peak around

588ºC, corresponding to the presence of hydroxyls of the octahedral leaf; and exothermic peak around 932ºC, characterizing the nucleation of mullite by the high kaolinite content, as we will see in the XRD tests. From the TG curves, we observed that the total loss of mass was of 17.2%, corresponding to the losses of water, organic matter and hydroxyl. Comparing the result of the thermogram with the values found in previous studies [1,7,10,11],we observe that the studied clay present thermal behavior similar to the those seen the analyses of bentonite clays..

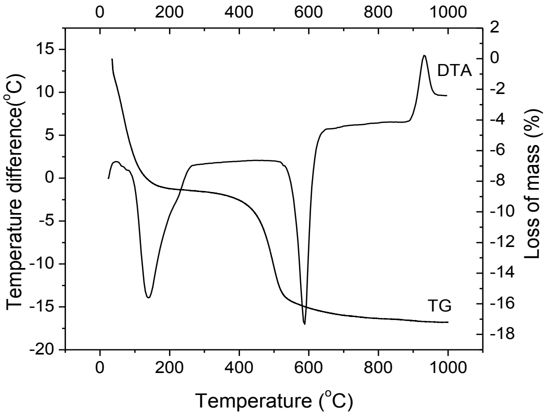

Figure 2. Thermogram of the Superior Gray bentonite.

Characterization of the samples purified by sieving and by hydrocycloning

Figure 3 and Table 3 present the results of the granulometric analyses by laser diffraction of the purified clay (overflow) with use of sieves (SG-325) and purified through sieving followed by hydrocycloning in a given configuration (SG-325-A1). Analyzing Table 3, we see that the clay, after purification by sieving only, presented a concentration of particles sizes between 3 and 9µm, obtaining a mean diameter for smaller particles of 4.75µm for the Superior Gray clay purified by sieving and then by hydrocycloning (SG-325-A1-OF), and larger of 7.41µm for the Superior Gray clay purified just by sieving (SG-325). We could also notice a high percentile accumulated volume with diameter below 2.0µm, equivalent to 22.34% for the SG-325-A1-OF sample, corresponding to the clay content, and 17.88% for SG-325.

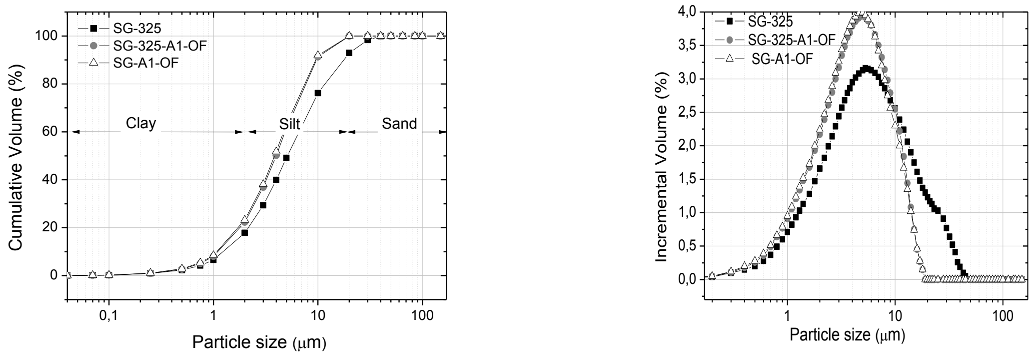

Figure 3. Result of the granulometric analysis of the Superior Gray clay purified by sieving.

For the results of the granulometric analyses of the purified clay (overflow) by hydrocycloning in the six configurations, we see that the purification by hydrocycloning presented a concentration of particles sizing between 3 and 7µm, obtaining a smaller particles mean diameter of 4.58µ for the SG-A3-OF sample, and larger of 5.09 for the SG-B3-OF sample. We were also able to notice that the highest percentage of accumulated volume with mean diameter below 2.0µm, equivalent to 24.53%, is found in the sample purified with hydrocyclone in the configuration A3 (SG-A3-OF), which corresponds to the clay content, and 21.07% for the SG-B3-OF. For the accumulated silt content, particle diameter above 2µm and below 20µm, all purified samples we superior to 70.0%.

Table 3. Granulometric distribution by sieving and by hydrocycloning of the clays from Cubati, PB.

Samples	*Clay (%) (x<2μm)*	*Silt (%) (2μm<x<20μm)*	*Sand (%) (x>20μm)*	*Mean diameter (μm)*
Superior Gray	11.96	76.53	11.51	9.19
SG-A1-OF	23.21	76.79	0	4.63
SG-A2-OF	23.35	76.65	0	4.71
SG-A3-OF	24.53	75.47	0	4.58
SG-B1-OF	21.76	78.24	0	4.84
SG-B2-OF	22.29	77.71	0	4.88
SG-B3-OF	21.07	78.81	0.12	5.09
SG-325	17.88	75.06	7.06	7.41
SG-325-A1-OF	22.34	77.66	0	4.75

SG – Superior Gray; OF – *overflow* (diluted suspension); 325 – passing through ABNT sieve no. 325.

A joint analysis of these results reveals that, among the purified samples, the A3 configuration is the one which resulted in the highest clay content (x<2μm). We also see that the sample subjected to purification by sieving and then by hydrocycloning (SG-325-A1-OF) presented inferior clay content with respect to the sample purified solely by hydrocycloning performed with the same configuration (SG-A1-OF). From these results, we clearly see the reduction of the mean equivalent size of particles after the hydrocycloning process, an increase in the clay content and a reduction of the sand content, which are characteristics that support the organofilization process.

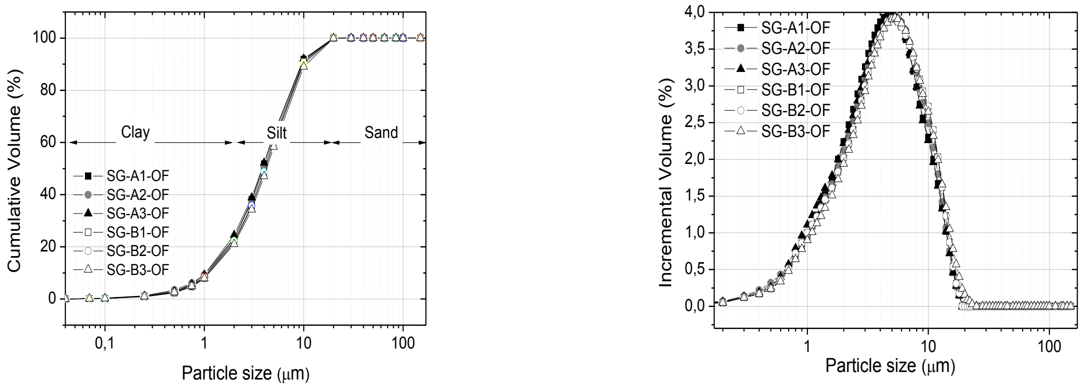

Figure 4. Result of the granulometric analysis of the Superior Gray clay purified by hydrocycloning in the six configurations.

Next we present the X-ray diffraction results for the clays from Cubati, PB, purified through: (a) sieving, where the diffractogram of the Superior Gray clay pointed out the presence of smectitic clay mineral, characterized by the interplanar distances around 15-16Å and 2,52-2,56Å; kaolinite, characterized by the interplanar distances around 7,1Å, 4,4Å, 3,5Å, and quartz, characterized by the interplanar distances around 3,33Å, 2,33Å and 1,67Å; (b), purified by hydrocycloning in the six configurations, being observed the presence of smectitic clay mineral, characterized by the interplanar distances 15Å and 2,52-2,56Å; kaolinite, characterized by the interplanar distances around 7,1-7,3Å, 4,4Å, 3,5Å, and quartz, characterized by the interplanar distances around 3,33Å, 2,33Å and 1,67Å.

An analysis of pooled results shows that the efficiency of the purification process can be easily observed by granulometric analysis and X-ray diffraction, with noticeable reduction of the quartz peak in the samples.

Through the results of the characterizations of the purified samples, we notice that purification solely by hydrocycloning presents the best results, since it led to larger concentration of the clay content below 2μm.

Conclusions

Based on these results, we conclude that: the characterization tests by laser diffraction, EDX, XRD, DTA and TGA show that the sample is constituted by the clay mineral of the smectite group, kaolinite and the accessory mineral, quartz, and thus may be called bentonite; the characterization tests show that the purification using only the hydrocycloning process presents the best results; besides, we notice that by using the vortex of smaller internal diameter (5mm), we achieved a reduction of the cutoff diameter, so, the best configurations for the hydrocyclone are A1, A2 and A3, with superiority of the A3 configuration.

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