Studies of new occurrences of bentonite clays in the State of Paraíba for use in water based drilling fluids

Estudos de novas ocorrências de argilas bentoníticas do Estado da Paraíba para uso em fluidos de perfuração base água

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Resumo

Recentemente foram descobertos novos depósitos de argilas bentoníticas no Estado da Paraíba principalmente nos municípios de Cubati e Pedra Lavrada, criando uma grande expectativa pela possibilidade de ampliação das novas reservas para produção industrial. O objetivo desse trabalho foi estudar as novas ocorrências de argilas bentoníticas da Paraíba, principalmente do município de Pedra Lavrada, para uso em fluidos de perfuração base água. A caracterização mineralógica foi efetuada através da análise granulométrica por difração de laser, análises termogravimétrica e térmica diferencial, composição química por fluorescência de raios X, difração de raios X, capacidade de troca de cátions e área específica. As argilas bentoníticas foram tratadas com carbonato de sódio nas concentrações de 75, 100,125,150 e 175meq/100g de argila seca, para sua transformação da forma policatiônica para forma sódica. Para caracterização tecnológica, foram confeccionados fluidos de perfuração de acordo com as normas da Petrobras. Os resultados obtidos evidenciaram que as amostras estudadas apresentaram, na sua composição mineralógica, montmorilonita, caulinita e quartzo. Em relação às propriedades reológicas, verificou-se que as amostras estudadas atendem parcialmente aos requisitos reológicos da norma da Petrobras.

Palavras-chave: Argila bentonítica, caracterização, fluidos de perfuração.

Abstract

New bentonite clay deposits have recently been discovered in the state of Paraíba, mainly in the municipalities of Cubati and Pedra Lavrada, creating great expectations in view of the possibility of expanding industrial production using these new reserves. The aim of this study was to study the new occurrences of bentonite clay in Paraíba, particularly in the municipality of Pedra Lavrada, for use in water based drilling fluids. The mineralogical properties of the clays were characterized by particle size analysis using laser diffraction, and thermogravimetric and differential thermal analysis, and its chemical composition was analyzed by X-ray fluorescence, X-ray diffraction, cation exchange capacity and specific surface area. The bentonite clays were treated with sodium carbonate at concentrations of 75, 100, 125, 150 and 175mEq/100g of dry clay, to transform them from polycationic to sodium form. For the technological characterization, drilling fluids were prepared according to the standards of Petrobras. The results indicated that the mineralogical composition of the samples consisted of montmorillonite, kaolinite and quartz. As for their rheological properties, the samples were found to partially meet the rheological requirements of the Petrobras standard.

Keywords: *Bentonite clay, characterization, drilling fluids.*

1. Introduction

The crystalline structure of bentonite clays is triple-layered, consisting of two tetrahedral sheets and one octahedral sheet. These tetrahedral and octahedral sheets exhibit isomorphic substitution that produces a charge imbalance, generating a cation-exchange capacity (CEC) in the order of 100mEq/100g of dry clay. This group comprises four dioctahedral and three trioctahedral clay minerals. The dioctahedral clay minerals are beidellite, nontronite, volkonskoite and montmorillonite, and the trioctahedral clay minerals are saponite, sauconite and hectorite (Souza Santos, 1992; Silva and Ferreira, 2008 and 2009).

Bentonite clays are produced by the decomposition of volcanic ash in alkaline environments with restricted water circulation, and their predominant clay mineral is montmorillonite (Souza Santos, 1992; Silva and Ferreira, 2008 and 2009).

It should be noted that bentonites are composed mainly of the clay mineral montmorillonite. The complexity of these concepts leads to constant misinterpretation. To further complicate the issue, Souza Santos (1992) stated that montmorillonite clays used industrially as bentonites, regardless of their geological origin, can be called bentonites. In the same vein, we should mention the work of Golpinath, Schuster and Schuckmann (1981 and 1988), who showed that montmorillonite clays from the region of the municipality of Boa Vista, state of Paraíba, and surroundings are bentonites. Thus, in this paper, the clays under study will be referred to as bentonites.

Bentonite may be calcium or sodium bentonite, and in its sodium form it presents a very particular physical characteristic, i.e., its volume expands many times over when in contact with water, forming thixotropic gels (Souza Santos, 1992; Bernier et al., 2003; Sousa, 2010; Menezes et al., 2008).

Bentonite is used industrially for various purposes, e.g., as a viscosity modifier of oil drilling fluids, as a sand casting binder, as an iron ore pelletizer, in sanitary napkins for pets, and as an oil bleacher, among others uses (Caenn and Chillingar, 1996; Mahto and Sharma, 2004; Amorim et al., 2002; Coelho and Souza Santos, 2007; Campos 2007; Menezes et al., 2009; Menezes et al., 2010).

Several researchers of the Academic Unit of Materials Engineering at the Federal University of Campina Grande – UFCG, Brazil have been conducting research into the use of bentonite clay in oil drilling fluids. These studies include that of Amorim (2003), who worked on samples of natural bentonite clays and industrialized sodium clays from deposits in Boa Vista, PB, aiming to improve their rheological behavior and obtain contamination resistant water and clay-based fluids. The results indicated that the different behaviors presented by dispersions, after protection and recovery treatments, can be very useful to optimize the application of these clays in drilling fluids.

Campos (2007) studied compositions of bentonite clays in deposits in the municipality of Boa Vista, PB, aiming to potentiate the utilization of poor quality clays in oil drilling fluids. The results confirmed that studies of clay compositions can be very useful for the clay miners and beneficiation industry of Boa Vista, as well as for the crude oil sector, given the possibility of using poor quality clay, which is available in large quantities in bentonite deposits, in oil drilling fluids.

Sousa (2010) studied compositions of organophilic clays for organic based drilling fluids containing the following additives: dispersants, emulsifiers, brine, activator, filtrate reducer, and densifiers, in order to evaluate their rheological behavior, filtration and electrical stability. The results demonstrated that two of the developed compositions show a promising potential that meets the specifications of Petrobras.

Ferreira (2009) studied the organophilization of bentonite clays from Boa Vista, PB, for use as viscosity modifiers of oil-based drilling fluids. His findings indicated the importance of process variables to the organophilization process and the rheology of dispersions for use in drilling fluids.

The objective of this work was to study the new occurrences of bentonite clays in the municipality of Pedra Lavrada, state of Paraíba, Brazil, for use in water based drilling fluids.

2. Materials and methods

Materials

The following clay samples were used: Grey Clay, Light Clay, Green Clay and Dark Bentonite Clay, from deposits located in the municipality of Pedra Lavrada, PB.

Methods

The samples were dried at room temperature for approximately four days, after which they were milled in a ball mill lined with a very hard ceramic material. The milled materials were then sifted through an electric sieve (Pavitest I-3007) (0.074 mm sieve opening). Aliquots of the sifted materials were removed for the various physical, chemical, and mineralogical characterizations, and to test their use in water based drilling fluids.

The clays were characterized using the following techniques: laser diffraction particle size analysis (CILAS 1064 L/D particle size analyzer); thermogravimetric analysis (TGA) and differential thermal analysis (DTA) (BP Eng. Ind. e Com. Model RB 3020 thermal analyzer); chemical composition by X-ray fluorescence (EDX) equipment (Shimadzu EDX-720 fluorescence spectrometer), X-ray diffraction (Shimadzu XRD-6000 X-ray diffractometer); cation exchange capacity (CEC) and specific surface area (SSA) (using the methylene blue adsorption method described by Chen et al., 1974).

After the characterization tests, the bentonite clays, which naturally contain many different cations, were transformed into sodium bentonite by contact with concentrated sodium carbonate (Na_2CO_3) solutions in the following concentrations: 75, 100, 125, 150 and 175mEq/100g of dry clay. The degree of fineness and moisture content were then determined.

The rheological properties of apparent viscosity (AV) and plastic viscosity (PV) were determined, using a Fann 35A viscometer. Filtrate volume was determined by filtration through a Fann filter press, and pH in a Hanna electronic pH meter. All the tests were performed according to the Petrobras EP-1EP-00011-A standard (2011).

3. Results and discussion

Table 1 and Figure 1 describe the particle size distribution of the clays under study, whose distribution curve is monomodal (Gray and Light Clays) or bimodal (Green Clay and Dark Bentonite). The latter show a concentration of particles between 2 and 9 μm, with a mean diameter smaller than 3.29 μm for the Grey Clay and larger than 12.25 μm for the Dark Bentonite.

In addition, a high cumulative volume percentage was found to have a mean diameter smaller than 2.0 μm, which was equivalent to 47.0% for the Green Clay (corresponding to the clay fraction) and to only 9.0% for the Dark Bentonite Clay. In terms of accumulated volume of silt (particle diameter larger than 2μm and smaller than 20μm), the Light and Dark Bentonite clays showed values above 71.0%, while the Green and Gray clays showed lower values of 44.0% and 54.0%, respectively.

A comparison of the particle size distribution reported by Ferreira (2009) for Chocolate Bentonite clays from Boa Vista, PB, and the Light clay from Pedra Lavrada,PB, reveals very similar results, thus indicating that the physical characteristics of this sample will probably be similar to those of the bentonites from Boa Vista, PB.

Figure 2 shows the TGA and DTA curves of the clays of this study. An

Samples	Clay (%) (x<2μm)	Silt (%) (2μm<x<20μm)	Sand (%) (x>20μm)	Mean Size (μm)
Grey Clay	45,88	53,97	0,15	3,29
Light Clay	19,03	74,68	6,29	7,35
Green Clay	47,23	43,99	8,78	6,27
Dark Bentonite Clay	9,26	71,03	19,71	12,25

Table 1
Particle size distribution and average particle diameter of the samples.

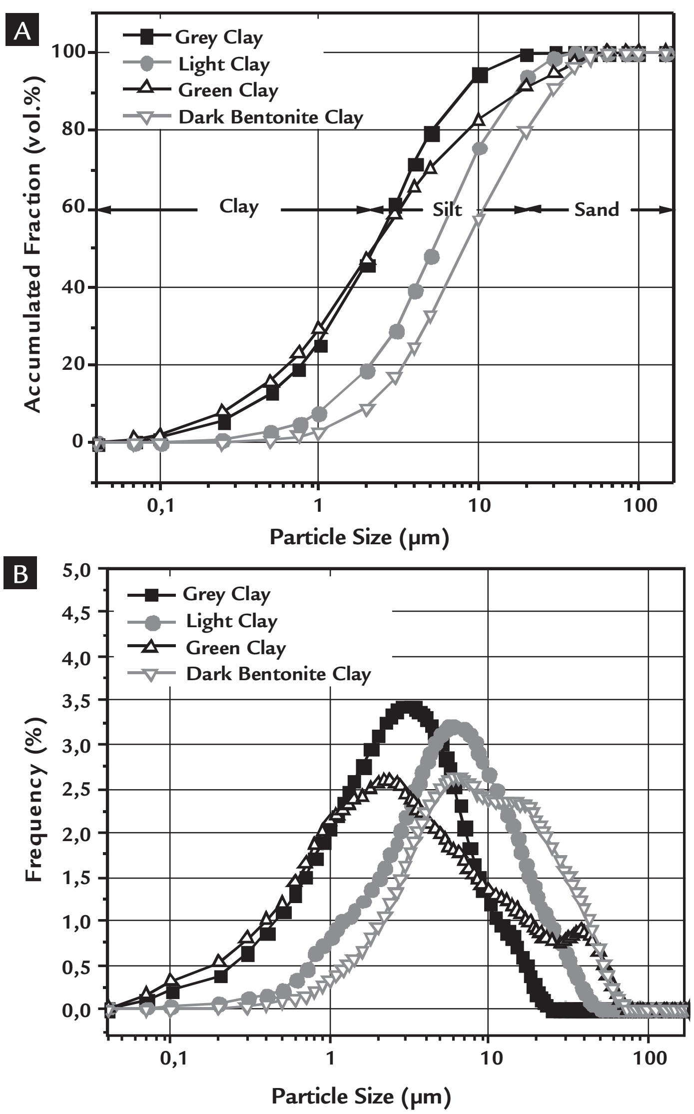

Figure 1
Particle size distribution of the clays: cumulative volume (A), histogram (B).

analysis of the curves in Figure 2A reveals the following thermal transformations: an endothermic peak at around 150°C, characterizing the presence of free and adsorbed water; an exothermic band between 200 and 500°C, corresponding to the combustion of organic matter (in the Gray and Light clays); an endothermic peak at around 520°C, characterizing the presence of hydroxyls and an exothermic peak at around 930°C, characterizing the nucleation of mullite due to the high kaolinite content, as will be seen in the XRD tests. The TGA curves in Figure 2B indicate total mass losses of 17.6%, 19.2%, 18.8% and 19.5%, respectively, which correspond to losses in water, organic matter and hydroxyls. A comparison of the results of our thermogravimetric analysis with those reported by Menezes et al. (2009) for bentonites from Cubati, PB shows that they are similar.

Table 2 presents the chemical compositions of the samples under study. An analysis of the results in Table 2 indicates that the clays had high SiO_2 (> 45%) and Al_2O_3 (> 25%) contents. The Gray and Green Clays presented 6.9% and 7.0% of Fe_2O_3 content, respectively, while that of the other clays was lower than 5.0%.

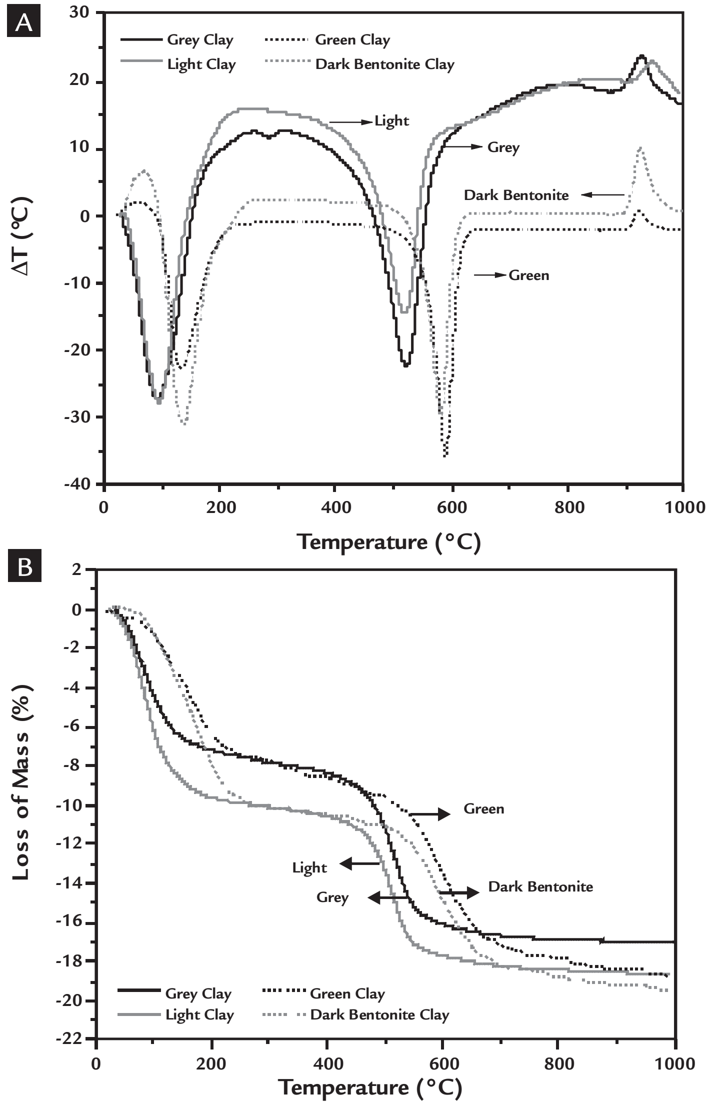

Figure 2
Thermal analysis
of the samples:
A) DTA,
B) TGA.

Table 2
Chemical composition
of the samples under study.

	Grey Clay	Light Clay	Green Clay	Dark Bentonite Clay
SiO_2	49,4	55,0	44,3	45,2
Al_2O_3	31,4	30,0	25,0	27,8
Fe_2O_3	6,9	3,2	7,0	3,9
MgO	1,8	2,2	1,9	2,0
CaO	0,1	0,5	0,0	0,4
K_2O	0,6	0,5	1,7	0,3
TiO_2	1,3	1,0	0,8	0,9
LOI*	8,0	7,3	18,8	19,5
Others	0,6	0,3	0,6	0,1

*LOI – Loss on Ignition

According to Amorim (2003), an iron content of about 7.0% is typical of clays from the municipality of Boa Vista, PB. Souza Santos (1992) stated that these iron contents come from bentonite containing about 4.0 to 6.0% of Fe_2O_3. The K_2O and TiO_2 contents were relatively low, i.e., lower than 2%. Comparing the values reported by Amorim (2003) and Souza Santos (1992), we found that the chemical composition of the clays is typical of bentonite clays.

Figure 3 presents the XRD results of the clays studied here. Figure 3 shows that the samples presented the following mineral phases: smectites (montmorillonite), characterized by 15.201Å, 4.48Å and 3.050Å; kaolinite, characterized by interplanar distances of 7.15Å, 3.566Å, 3.365Å, 2.553Å, 2.331Å and 1.892Å; and quartz, characterized by 4.26Å, 2.166Å, 1.817Å and 1.672Å. The presence of smectite (montmorillonite) was confirmed by testing with ethylene glycol (Souza Santos, 1992). Thus, it can be stated that, in general, these clays contain large quantities of kaolinite. The Dark Bentonite clay sample showed a slightly lower kaolinite content, which may favor its rheological behavior.

According to Menezes et al. (2009), bentonite clays from the municipality of Cubati, PB present the following mineral phases: montmorillonite, kaolinite and quartz, and are similar to the clays from the municipality of Pedra Lavrada. In general, the Grey, Light, Green and Dark Bentonite clays presented XRD patterns typical of bentonite clays with high kaolinite contents (Souza Santos, 1992; Ferreira, 2009).

Table 3 describes the cation exchange capacity (CEC) of the samples under study, which was determined by the methylene blue method. As can be seen in Table 3, the CEC values of the samples were very similar, except for the Grey clay sample, and were lower than the level of montmorillonite clay mineral in the smectite group due to their high kaolinite content (80 to 150mEq/100g) (Souza Santos, 1992). However, compared with the clays from the municipality of Boa Vista, PB, whose CEC is 56 meq/100g, according to Ferreira (2009), the results of this study were very similar, i.e., CEC values of 60 to 64 mEq/100 g.

Table 4 shows the results of the specific surface area of the samples. In Table 4, note that the specific surface area of all the samples exhibited higher values than those of the montmorillonite clays studied by Ferreira (2009). According to Ferreira (2009), the specific surface area of chocolate type smectite clays from the municipality of Boa Vista, PB, is 437.04 m^2/g. Comparing this value with that of the clays in the municipality of Pedra Lavrada, PB, one finds that the Green and Dark Bentonite clays possess higher values of specific surface area.

Table 5 shows the apparent viscosity (AV), plastic viscosity (PV), pH, filtrate volume, degree of fineness and moisture content of the clay samples. As can be seen in Table 5, the Dark Bentonite showed best results of apparent viscosity (AV), with values of 23 cP, 22 cP and 19.5 cP for contents of 75, 100 and 150 mEq/100g of dry clay. A comparison of these values with the Petrobras standards (2011) indicates that the AV is higher

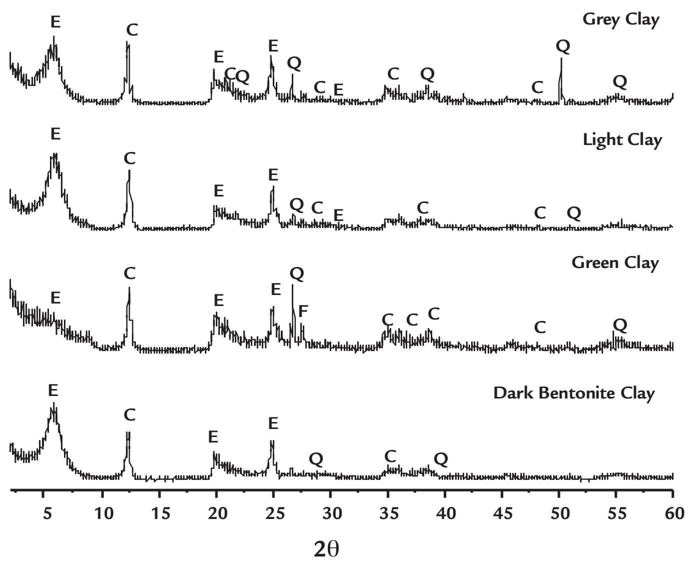

Figure 3
X-ray diffractograms of the clays.

Clays	Cation exchange capacity (meq/100g)
Grey Clay	56
Light Clay	60
Green Clay	64
Dark Bentonite Clay	64

Table 3
Cation exchange capacity of the samples.

Amostras	Specific surface area (m^2/g)
Grey Clay	437,04
Light Clay	468,26
Green Clay	499,47
Dark Bentonite Clay	499,47

Table 4
Specific surface area of the samples.

than the minimum specified apparent viscosity of 15.0 cP. As for plastic viscosity (PV), which, according to Petrobras specifications (2011) cannot be lower than 4.0 cP, the Grey clay presented the best results, i.e., a concentration of 150 mEq/100g. In terms of pH, all the clays are very close to Petrobras specifications (2011) which require a maximum of pH 10.0. The filtrate volume exceeded the 18.0 mL specified by the Petrobras standards (2011).

After sifting the samples though an ABNT # 200 mesh sieve (0.074 mm), the sieve residue was lower than the maximum of 4.0% specified by Petrobras. The moisture content of the clays was lower than the maximum of 14.0% required by the specifications. An overall analysis of the results indicated that none of the samples meets the requirements of Petrobras (2011), and that the dark bentonite clay presented the best results. However, the results of all the samples need to be studied in greater depth, particularly with respect to their rheological properties with additives. According to the studies of Amorim (2003), encouraging results have shown that, with industrial additives, it is likely that suitable responses can be obtained for clay dispersions in the flocculated gel state, which is the case of Dark Bentonite, with an increase in apparent and plastic viscosity and reduction of the filtrate volume, in order to meet the requirements of the standard.

Table 5
Apparent viscosity (AV), plastic viscosity (PV), filtrate volume, degree of fineness and moisture content of the samples.

Samples	Na_2CO_3 meq/100g	AV (cP)	PV (cP)	pH	Filtrate volume (mL)	Degree of fineness	Moisture content (%)
Grey Clay	75	7,0	3,0	10,45	39,2	0	4,7
	100	6,0	2,0	10,49	45,6	0	4,7
	125	6,0	3,0	10,60	48,7	0	4,7
	150	6,0	4,0	10,59	51,52	0	4,7
Light Clay	75	5,5	2,0	10,24	32,34	0	4,0
	100	3,0	2,0	10,40	31,2	0	4,0
	125	6,0	2,0	10,43	32,63	0	4,0
	150	6,0	2,0	10,41	35,77	0	4,0
Green Clay	75	1,5	1,0	10,68	39,50	0	6,7
	100	0,5	0,0	10,61	52,38	0	6,7
	125	1,0	1,0	10,61	51,23	0	6,7
	150	1,5	1,0	10,57	58,67	0	6,7
Dark Bentonite Clay	75	23,0	2,0	9,84	35,77	0	7,3
	100	22,0	1,0	10,22	38,35	0	7,3
	125	17,0	2,0	10,26	38,64	0	7,3
	150	19,5	2,0	10,52	41,50	0	7,3

4. Conclusões

Based on this study of new occurrences of smectite clays in the municipality of Pedra Lavrada, PB for possible application in water based drilling fluids, it was concluded that the samples presented a mineral composition of montmorillonite, kaolinite and quartz. As for their rheological properties, the samples partially meet the specifications of Petrobras standards (2011) for use in water based drilling fluids, and the Dark Bentonite Clay was found to be the most promising sample.

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