

Influence of Ca²⁺ in the rheological properties and filtration of bentonitic clay dispersions in aqueous drilling fluids

(Influência do Ca²⁺ nas propriedades reológicas e de filtração de dispersões de argilas bentoníticas em fluidos de perfuração aquosos)

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Abstract

The physicochemical characteristics of cations may be able to modify the rheological properties of bentonite clays, such as their loads, exchangeable cation sizes adsorbed on clay minerals, hydration behaviors and different intercalations with the bentonite structural layer effect of the cations present on the rheology of dispersions of bentonite clays. In this way, the objective was to study the influence of Ca²⁺ on the rheological and filtration properties of dispersions of new occurrences of bentonite clays from the State of Paraíba, Brazil, in aqueous drilling fluids. Four bentonite clays were selected, being characterized chemically, physically and mineralogically. Sodium carbonate was then added to the clays, and the rheological and filtration behavior of their dispersions were studied. The results showed the direct influence of the Ca²⁺ present and its implications, resulting from physicochemical interactions, on the rheological and filtration properties of dispersions of bentonite clays.

Keywords: bentonite clays, calcium ion, rheological and filtration properties, drilling fluids.

Resumo

As características físico-químicas dos cátions podem ser capazes de modificar as propriedades reológicas das argilas bentoníticas, como suas cargas, tamanhos dos cátions trocáveis adsorvidos nos argilominerais, comportamentos de hidratação e diferentes intercalações com as camadas estruturais da bentonita, sendo um fator importante considerar o efeito dos cátions presentes sobre a reologia de dispersões de argilas bentoníticas. Desta forma, o objetivo desse trabalho foi estudar a influência do Ca²⁺ nas propriedades reológicas e de filtração de dispersões de novas ocorrências de argilas bentoníticas do estado da Paraíba, Brasil, em fluidos de perfuração aquosos. Quatro argilas bentoníticas foram selecionadas, sendo caracterizadas química, física e mineralogicamente. As argilas foram aditivadas com carbonato de sódio e estudados os comportamentos reológicos e de filtração de suas dispersões. Os resultados mostraram a influência direta do Ca²⁺ presente e suas implicações, resultantes de interações físico-químicas, nas propriedades reológicas e de filtração de dispersões de argilas bentoníticas.

Palavras-chave: argilas bentoníticas, íon de cálcio, propriedades reológicas e de filtração, fluidos de perfuração.

INTRODUCTION

The smectic clays are materials consisting of one or more clayey smectite and some accessory minerals. The clay minerals are the main solid constituents of cohesive soils, dispersed sediments and some fine-grained rocks, being one of the most important mineral resources used in many industrial and domestic applications. The smectite sand-minerals are aluminosilicates of sodium, calcium, magnesium, iron, potassium and lithium, which include: montmorillonite, nontronite, saponite, hectorite, sauconite, beidellite and volkonskoite. The montmorillonite is the predominant clay in the bentonite clays, having a layered structure, being an octahedral layer of aluminum hydroxide [Al(OH)₃] between two tetrahedral layers of silica (SiO₂).

Their hexagonal plates carry a negative surface charge due to the isomorphic substitution in Al³⁺ metal centers in the layers by lower valence metal ions, such as Fe²⁺ and Mg²⁺, and is widely surrounded by exchangeable cations such as Na⁺, H⁺, K⁺ and Ca²⁺, balancing the responsible network. In this sense, smectic clays can vary greatly in relation to their physical, chemical and mineralogical composition, where this variation depends on their geological formation, which can greatly compromise their industrial application [1-5].

The search for new occurrences of bentonite clays in the State of Paraíba, Brazil, has become more and more important since, due to the disordered extraction of the bentonite clays in this State, the clays of the best mineralogical compositions have been depleted [4, 6]. Mineral accessories (mainly quartz, cristobalite, mica, calcite, dolomite and feldspars) compromise the technological applications of bentonite clays, mainly their rheological properties that are greatly found in clays commercialized today, which makes

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it increasingly necessary to discover new occurrences of bentonite clays [7-9]. For aqueous drilling fluids, it is essential that there be an interaction between the clay and the water in the dispersions, for the formation of the double electric layer on the clayey surfaces and expansion of the hydrated layers. From these interactions, the intercalation of water into clay minerals may cause an initial increase in particle thickness, which may result in an increase or decrease in size depending on the types of intercalation cations or degree of swelling and other environmental conditions [1, 10-12]. Another important issue is the stability of the clay dispersion; an unstable dispersion can lead to aggregation of particles, resulting in a coarser particle size distribution, thereby altering the particle size distribution. The use of chemical dispersants is important in obtaining deflocculated mineral dispersions [3, 12].

In general, Brazilian bentonite clays are polycationic, with a predominance of calcium due to the formation or geological origin, and traditionally they are transformed into sodium by the addition of sodium carbonate (Na_2CO_3) [4-8, 13]. The presence of clays in the calcic and polycationic form leads to unsatisfactory rheological results. In the process of cation exchange, Na^+ ions traditionally substitute Ca^{2+} ions, leading to a better condition in the deflocculation state, resulting in suitable rheological properties for the use of sodium nitrite clays as a key component in waterborne drilling fluids. In addition to structural or substitutional Ca^{2+} , there may also be contamination of bentonite clays during industrial processing, due to the high turnover of mills for materials of different compositions [6]. The cation exchange reactions are selective, with a predominance of empirical data in the current context. Some preference orders are related, such as Li^+ , Na^+ , K^+ , Cs^+ , Mg^{2+} , Ca^{2+} , Fe^{2+} [2, 13]. It is thus observed that calcium clays, because they are not in the foreground of selectivity, lead to unsatisfactory rheological results [2, 13-15]. Therefore, the existence of numerous limestone deposits is a challenge, requiring more and more studies that point out their characteristics for the most diverse industrial applications. Thus, it is essential to study the influence of Ca^{2+} on the rheological and filtration properties of dispersions of bentonite clays in aqueous drilling fluids.

MATERIALS AND METHODOLOGY

For this study, four bentonite clays, named clays A, B, C and D, were selected from the municipalities of Olivedos and Cubati, PB, Brazil, where new deposits of bentonite clays were discovered. Clays B and D underwent an industrial milling process, ABNT No. 200 (0.074 mm) sieve, while clays A and C were milled in a laboratory. Sodium carbonate (Na_2CO_3) PA, purity of 99.5% (Labsynth, Diadema, Brazil), was used in the additivation of the clays. The preparation and processing of the samples for characterization tests were done by a ball mill and ABNT No. 200 sieve (0.074 mm). The samples were physically, chemically and mineralogically characterized by the following techniques: i) X-ray

diffraction (XRD 6000, Shimadzu), to evaluate the changes in the interplanar basal distance d_{001} ; all samples were tested with and without addition of ethylene glycol to confirm the clays of the smectite group; the test was conducted using $\text{CuK}\alpha$ radiation, fixed-time scanning mode (step of 0.02° 2θ and counting time of 0.6 s) in the range 5° - 60° for natural and sodium samples, and with a range of 5° - 10° for samples with ethylene glycol saturation, 0.5° divergence, anti-scatter slits and 0.15 mm receiving slit, using 40 kV/30 mA monochromator; the window of experimental error was about $\pm 0.03 \text{ \AA}$ at 2θ of 28.2° ; ii) X-ray fluorescence chemical analysis (EDX 720, Shimadzu); iii) granulometric analysis by laser diffraction (AG, 1064, Cilas) using 5 g of clay for 8.9 mL of sodium hexametaphosphate, with a velocity of 17000 rpm per 10 min, in a humid mode (250 mL of distilled water), until reaching the ideal concentration that was 170 diffraction units/incidence area; iv) thermal curves were obtained using the differential thermal analysis (DTA) system and thermogravimetry (TG, RB-3000, BP Eng.), maximum temperature of 1000°C , and the reference used in the DTA was calcinated aluminum oxide (Al_2O_3) in an air atmosphere, with a heating rate of $12.5^\circ\text{C}/\text{min}$; and v) cation exchange capacity (CEC) and specific surface area (SA) were determined by the methylene blue adsorption method [16]; the solution of methylene blue with 0.01 N concentration and dry clay mass of 0.5 g (ABNT No. 325 sieve) was prepared with 300 mL of deionized water under mechanical agitation, with CEC presented in meq/100 g of dry clay and SA in m^2/g .

The process of additivation used to modify the polycationic samples in monocationic was carried out taking into consideration the CEC moisture of the bentonite clays in use, calculating the gram equivalent and the milligram unit of the carbonate involved. Using the mass of the sample (dry clay) used, the mass of sodium carbonate required to add to the clay was calculated [6]. Water was then added so that an ideal humidity of 30%-40% was reached and placed in closed bags during 5 days for curing so that the additive process was effective [2, 6]. After the curing period, the rheological and filtration behaviors were studied. The polycationic and monocationic bentonite dispersions were prepared at the concentration specified by Petrobras [17], 24.3 g/500 mL of deionized water (4.86% by mass), then homogenized in the Marconi 500 W agitator at approximately 150000 rpm for 20 min, shortly after standing for 24 h. The rheological parameters, apparent viscosity (AV) and plastic viscosity (PV), were measured by means of the Fann 35A viscometer according to:

$$AV = 300 \frac{\theta}{N} \quad (\text{A})$$

where AV is the apparent viscosity (mPa.s), N is the rotational speed at 600 rpm of the Fann viscometer and θ is the deflection measured in the viscometer at this speed;

$$PV = 300 \frac{\theta_2 - \theta_1}{N_2 - N_1} \quad (\text{B})$$

where PV is the plastic viscosity (mPa.s), θ_2 and N_2 with reading at 600 rpm and θ_1 and N_1 with reading at 300 rpm. The filtrate volume (FV) was determined by a filter press test, in which the dispersion was inserted and the filtrate collected over the period of 30 min after the application of a pressure of 690 ± 35 kPa (100 ± 5 psi). The water-based fluids obtained then followed Petrobras' viscosifier standardization for fluids used in the exploration and production of oil and gas wells.

RESULTS AND DISCUSSION

Fig. 1 shows the XRD patterns of polycationic and monocationic clays A, B, C and D with and without ethylene glycol. The following mineralogical phases were observed: smectite (JCPDS 10-0357), characterized by reflections at 15.20 and 4.48 Å; kaolinite (JCPDS 78-2110) at 7.14, 3.365 and 2.55 Å; quartz (JCPDS 46-1045) at 4.26, 3.34, 2.16, 1.81 and 1.67 Å; and calcite (JCPDS 05-0586) at 3.01 Å with higher peak intensities in samples B and D. In Fig. 1, the red curves indicate the characteristic peak of the smectite with the addition of ethylene glycol, confirming that the samples are, in fact, bentonite clays. In general, X-ray diffraction patterns confirmed qualitatively that the clays presented typical patterns of bentonite clays with other accessory minerals, especially calcite, similar to other studies [4, 6-8, 15, 18, 19]. The presence of calcite in the samples B and D indicated that these clays may have originated from

limestone formations [6], that is, higher levels of calcite can occur depending on the formation or geological origin of the clays, interfering with their properties, whether chemical or rheological.

Table I presents the results of the chemical composition of the polycationic and monocationic (additive) samples A, B, C and D. It was observed that the results obtained presented SiO_2 contents in the range of 47%-51% and 18%-22% Al_2O_3 , from the tetrahedral and octahedral sheets; 6%-8% Fe_2O_3 and 2%-3% MgO , resulting from isomorphous substitutions occurring in the octahedral sheet; 3%-4% Na_2O due to the process of additivation with the carbonate Na_2CO_3 ; 1%-6% CaO and 0-1% K_2O , among other oxides, where CaO was significant in samples B and D, confirming the results of XRD (Fig. 1), since different location extraction resulted in different chemical compositions [2, 6]. The results presented are typical of the clays of the State of Paraíba [2, 6-8].

Table II shows the granulometric distribution of the polycationic samples A, B, C and D. Analyzing the results obtained, we observed a decrease in the fraction $x < 2 \mu\text{m}$ and an increase in the fraction $x > 20 \mu\text{m}$ and D_m (average diameter) of samples B and D when compared with samples A and C, showing an increase in the percentage of accessory minerals, mainly containing Ca^{2+} , as also indicated in the results of XRD (Fig. 1) and chemical composition (Table I). Samples A and C, whose presence of Ca^{2+} was lower, had a better particle size distribution, with higher percentage

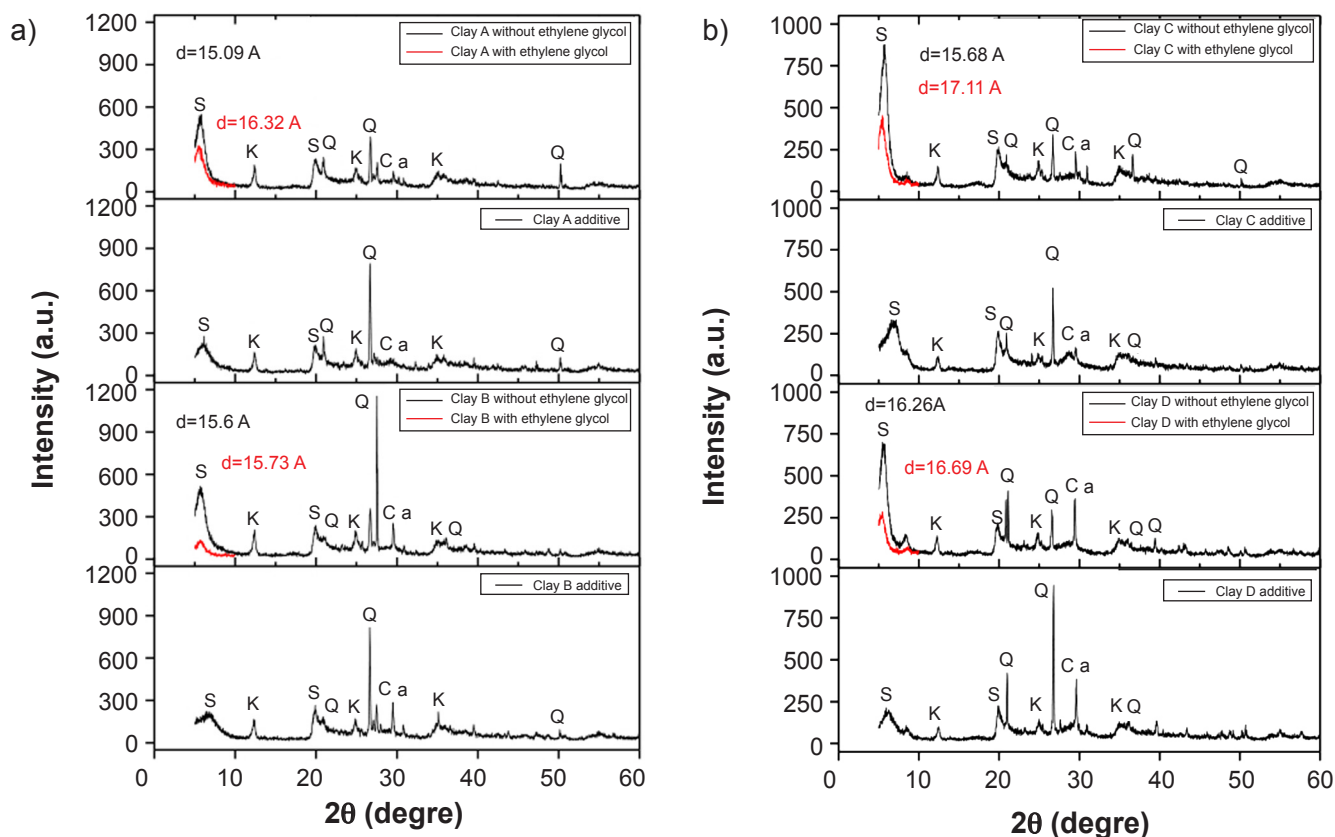


Figure 1: XRD patterns of the studied samples. S-smectite, Q-quartz, K-kaolinite, Ca-calcite.

[Figura 1: Padrões de DRX das amostras em estudo. E-smectita, Q-quartzo, C-caulinita, Ca-calcita.]

Table I - Chemical composition (wt%) of the samples under study.

[Tabela I - Composição química (% em massa) das amostras em estudo.]

Sample	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MgO	CaO	Na ₂ O	K ₂ O	TiO ₂	Others	LOI
Clay A	48.89	22.92	8.80	2.81	1.78	–	1.48	0.78	0.34	12.20
Clay A additive	47.07	21.08	8.82	2.84	1.80	4.02	1.51	0.79	0.31	11.63
Clay B	48.91	22.65	6.25	2.33	4.27	–	1.40	0.66	0.57	12.96
Clay B additive	47.38	21.95	6.28	2.42	4.28	3.99	1.43	0.69	0.55	11.03
Clay C	51.36	22.85	7.68	3.32	1.84	–	0.53	1.13	0.19	11.10
Clay C additive	50.08	21.01	7.74	3.45	1.88	3.85	0.55	1.19	0.23	10.02
Clay D	48.97	19.95	6.71	3.12	6.48	–	0.46	0.80	0.52	12.99
Clay D additive	47.25	18.99	6.66	3.15	6.50	3.54	0.48	0.84	0.51	12.08

LOI: loss on ignition; – absent.

fractions $x < 2 \mu\text{m}$ and lower values of $x > 20 \mu\text{m}$ and Dm. These granulometric distributions are typical of bentonite clays in the State of Paraíba [2, 6, 14, 15].

Table II - Grain size distribution of the samples under study.

[Tabela II - Distribuição granulométrica das amostras em estudo.]

Sample	Dm (μm)	$x < 2 \mu\text{m}$ (%)	$2 < x < 20 \mu\text{m}$ (%)	$x > 20 \mu\text{m}$ (%)
Clay A	4.78	48.59	49.20	2.21
Clay B	6.64	25.99	68.08	5.93
Clay C	5.17	52.16	47.46	0.38
Clay D	6.66	33.48	64.49	2.03

DM: average diameter.

Fig. 2 shows the results of TG and DTA of the samples of the polycationic and monocationic samples. Analyzing the DTA curves, the following thermal transformations were observed: first endothermic peak at approximately 100 °C, characterizing the loss of water (free and adsorbed); subsequently, the curves presented an exothermic band around 180 to 450 °C, which characterized the loss of organic matter; and at around 500 °C, an endothermic peak was observed responsible for the loss of structural hydroxyls. Samples B and D showed an endothermic peak around 700 °C, characteristic of the presence of carbonates, probably calcite, also observed in the results of XRD (Fig. 1), chemical composition (Table I) and particle size distribution (Table II). It was also observed an exothermic peak with a maximum at 940 °C, characteristic of the nucleation of mullite with the release of β -quartz. Based on the TG curves, it was possible to observe total mass losses for the polycationic samples of 20.39%, 21.3%, 22.12% and 23.05%, respectively; the total mass losses of the additive samples were 18.26%, 19.11%, 21.12% and 20.52% for samples A, B, C and D, respectively, corresponding to losses of water, organic matter and hydroxyls. According to the results, it was verified that the clays in study presented thermal behavior similar to the bentonite clays of the State of Paraíba [2, 6-8, 14, 15].

Table III shows the cation exchange capacity (CEC) and specific area (SA) of the polycationic and additivated samples. Table III shows that the CEC and SA results of the polycationic samples varied between 52.0 and 64.0 meq/100 g and 405.82 and 499.48 m²/g, respectively. In the additivated samples, the variations were between 56.0 and

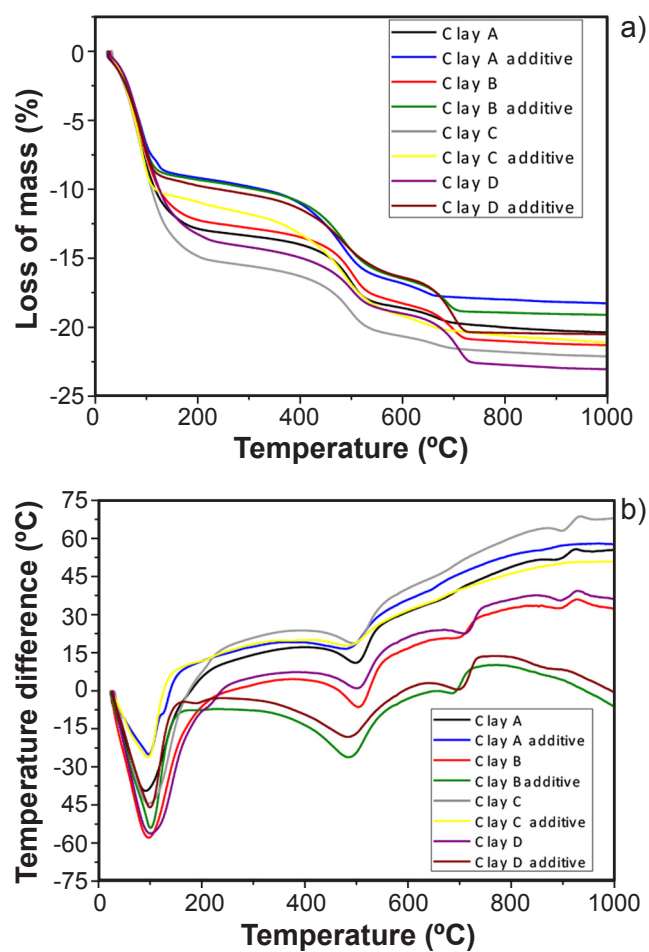


Figure 2: TG (a) and DTA (b) curves of the polycationic and monocationic (additive) samples.

[Figura 2: Curvas de DTA e TG das amostras policatiônicas e monocatiônicas aditivadas.]

76.0 meq/100 g for the CEC and 437.04 and 593.12 m²/g for the SA. It was possible to observe that the polycationic samples B and D presented lower values of CEC and SA than samples A and C, probably due to the presence of Ca²⁺, as observed in previous results (Figs. 1 and 2 and Tables I and II). However, the increase was subtler for samples B and D than for samples A and C, according to the values of the polycationic samples. Thus, it was possible to obtain a higher efficiency in the exchange of cations in samples A and C, with less amount of accessory minerals, since these samples also presented a larger fraction $x < 2 \mu\text{m}$ (Table II), thus containing a larger area of surface, and as such, facilitating the adsorption mechanisms of methylene blue molecules with montmorillonite clay minerals [2]. In addition, there was also a greater exchange between the cations in the clay particles and the carbonates of Na₂CO₃, facilitating the process of additivation and its industrial applications, such as rheological properties [2, 6]. In general, the influence of Ca²⁺ on the CEC and SA of the samples was observed, since the exchangeable ions strongly influence their physicochemical properties [6, 20], and it is, therefore, necessary to analyze if there is also influence on the viscosimetric and filtration properties of the dispersions obtained.

Table III - CEC and SA of the polycationic and additivated samples.

[Tabela III - CTC e AE das amostras policatiônicas e aditivadas.]

Sample	CEC (meq/100g)	SA (m ² /g)
Clay A	64.0	499.48
Clay A additive	76.0	593.12
Clay B	56.0	437.04
Clay B additive	60.0	468.26
Clay C	60.0	468.26
Clay C additive	72.0	561.91
Clay D	52.0	405.82
Clay D additive	56.0	437.04

Table IV shows the rheological (apparent viscosity - AV, plastic viscosity - PV) and filtration (filtrate volume - FV) results of the dispersions obtained with the polycationic and monocationic samples. It was observed that the rheological and filtration properties of the dispersions of samples before additivation did not reach the established specifications [17], presenting results below those specified. It can also be observed that, after additivation, the dispersions of the samples presented higher rheological and filtration results than when polycationic; this behavior can be explained due to the increase in CEC (Table III), probably due to higher electrostatic and mass interactions that form more rigid crosslinks, retaining the water molecules, thereby reducing the amount of free water in the system, increasing viscosity and decreasing filtration [21]. The dispersions of the additivated samples A and C conformed to standards

[17], whereas the dispersions of the additivated B and D samples only to AV specification, due to the higher amount of CaO, due to Ca²⁺ (Tables I and II), lower CEC (Table III), lower surface areas and lower cation exchange capacities, thus impairing its rheological and filtration properties. This behavior indicated that the presence of limestone accessory minerals, present in samples B and D, caused their dispersions to lead to unsatisfactory rheological results, showing a direct relationship with the previous characterization results of the clays (Figs. 1 and 2 and Tables I to III) [6, 22]. According to [23], drilling fluids undergo changes in their rheological behavior in the presence of contaminants, with apparent and plastic viscosities and filtrate volume being more compromised. It is important to highlight that even small amounts of carbonates and hydroxides can strongly influence the colloidal concentrations and rheological properties of clay dispersions [24]. These results are mainly explained by the physicochemical characteristics of the accessory minerals involved, such as those containing Ca²⁺ [13, 25, 26], which usually present bigger and higher density particles, reinforcing the assertions of the relationship of the granulometric distribution (Table II), whose particle size effect of clays is related to the viscosity and volume of filtrate [27]. Previous studies [2, 13, 24, 27-29] have shown that the type of cation present can affect the intercalation process by having different hydration and intercalation behaviors with the structural layers of bentonite, in which the force between cation and water connection decreases as the radius of the cation is increased; this means that the Na⁺ of the carbonate has a binding force with water greater than the Ca²⁺ present, either in the structure or acquired by contamination of calcareous lands or industrial processes, hydrating it more.

Table IV - AV, PV, FV of the samples.

[Tabela IV - VA, VP, VF das amostras.]

Sample	AV (mPa.s)	PV (mPa.s)	FV (mL)
Clay A	11.0	3.0	22.0
Clay A Additive	25.5	5.0	15.2
Clay B	6.5	2.5	28.5
Clay B Additive	17.0	3.0	23.5
Clay C	10.5	2.5	22.5
Clay C Additive	22.0	4.5	16.3
Clay D	6.0	2.0	35.0
Clay D Additive	15.5	2.5	29.5
Specification [17]	>15.0	>40	<18.0

AV - apparent viscosity; PV - plastic viscosity; FV - filtrate volume.

CONCLUSIONS

Based on the study of the influence of Ca²⁺ on the rheological and filtration properties of dispersions of new occurrences of bentonite clays from Paraíba State, Brazil, in

aqueous drilling fluids, it was concluded that the dispersions of bentonite clays with higher Ca²⁺ ion percentages had greater interferences in their cation exchange capacity (CEC) and rheological and filtration properties, proving the direct influence of the accessory minerals resulting from this ion in the physicochemical properties and rheology of dispersions of bentonite clays.

ACKNOWLEDGMENT

The authors would like to thank the CAPES (Coordination for the Improvement of Higher Education Personnel) for the financial support of the Brazilian research.

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(*Rec. 10/09/2018, Rev. 21/11/2018, Ac. 25/11/2018*)