Influence of the additivation process on cation exchange capacity and viscosity of bentonitic clay dispersions

(Influência do processo de aditivação na capacidade de troca de cátions e viscosidade de dispersões de argilas bentoníticas)

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Abstract

In Brazil, bentonite clays are not naturally sodic and it is an industrial practice the sodium additivation, since sodium ion expands their lamellae allowing a larger amount of water to penetrate. The objective was to analyze the influences of the use of sodium carbonate on the clay during the additivation process, the moisture content and the cure time on cation exchange and viscosity of bentonite clay dispersions for water-based drilling fluids, since there is a shortage of studies on this subject. Newly discovered bentonite clays in Paraíba State, Brazil, were chemically, physically and mineralogically characterized and were additivated with sodium carbonate in aqueous solution (process 1) or in powder form (process 2). Samples with 25% to 60% of moisture (dry basis) were prepared and submitted to cure times of 7 to 45 days. Process 1, as expected, showed better results of cation exchange capacity, viscosity and filtrate volume. The ideal cure time was 15 days. After this period there was a reversal of the cation exchange reactions.
Keywords: bentonite clays, additivation, cation exchange capacity, viscosity, drilling fluids.

Resumo

No Brasil, as argilas bentoníticas não são naturalmente sódicas e é uma prática industrial a aditivação sódica, uma vez que o íon de sódio expande suas lamelas permitindo a penetração de uma maior quantidade de água. O objetivo foi analisar as influências da adição do carbonato de sódio na argila durante o processo de aditivação, do teor de umidade e do tempo de cura na troca de cátions e viscosidade de dispersões de argilas bentoníticas para fluidos de perfuração à base de água, uma vez que há escassez de estudos neste tema. Argilas bentoníticas recém descobertas do estado da Paraíba, Brasil, foram caracterizadas química, física e mineralogicamente e aditivadas com carbonato de sódio em solução aquosa (processo 1) ou na forma de pó (processo 2). Amostras com 25% a 60% de umidade (base seca) foram preparadas e submetidas a tempos de cura de 7 a 45 dias. O processo 1, como esperado, apresentou melhores resultados de troca catiônica, viscosidade e volume de filtrado. O tempo de cura ideal foi de 15 dias. Após esse período houve reversão das reações de troca de cátions.
Palavras-chave: argila bentonítica, aditivação, capacidade de troca de cátions, viscosidade, fluidos de perfuração.

INTRODUCTION

Bentonite clays have received a prominent attention from researchers of different areas of knowledge, since these materials have numerous applications in the most varied industrial sectors [1-4], and can be defined in a simplistic way as a material consisting essentially of montmorillonite, which has a particle size of less than 2.0 μm [1, 5-7]. In addition, they have the chemical composition and formula of the 'theoretical' or extreme montmorillonite unit cell of the $(Al_{3.33}Mg_{0.67})Si_8O_{20}(OH)_4M^+_{0.67}$ series, where M^+ is a monovalent cation. This formula shows that the unit cell has a negative electric charge due to the isomorphic substitution of Al^{3+} by Mg^{2+}. The M^+ cation that balances the negative charge is called exchangeable cation, since it can be reversibly exchanged for other cations (depending on the cation). The exchangeable cation content, expressed in milliequivalents (meq) of the cation per 100 g of clay, is called cation exchange capacity (CEC). The stacking of the structural layers is governed by relatively weak polar and van der Waals forces and, between these layers, there are gaps called galleries or intermediary layers in which the exchangeable cations, such as Na^+, Ca^{2+}, and Li^+, are fixed electrostatically [1, 8]. The physicochemical properties of clay minerals are closely associated with surface and surface charge phenomena. Among these phenomena, there are the ability to exchange cations, the amphoteric character, and the surface acidity. On the charges resulting from isomorphic substitutions, the non-equilibrium dissociation of OH⁻ groups attracts especially exchangeable cations of

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different charges and sizes, which are adsorbed on the clay minerals, thus modifying the behavior for the technological and industrial level [9-11]. The CEC values after the cation exchange are strongly influenced by the diffusion coefficient of the medium in which the additive is placed, hence the dry-exchange process is replaced by the wet-exchange process [10, 11]. With such physicochemical versatility, bentonite clays have played an increasingly important role in many types of industrial applications, moving hundreds of millions of dollars into the global economy each year. Among these applications, this study highlights their use in aqueous drilling fluids [12-14].

Drilling fluids are primary suspensions of water and bentonite that play important roles in drilling wells [12, 15, 16]. Bentonite clays have been used for many years as a viscosifying agent in the composition of such suspensions and have various functions throughout the process. The success of drilling a well depends, among other factors, on the physical and chemical characteristics of the fluid used in the operation [12, 17, 18]. Their compositions are chosen to meet these characteristics, such as proper viscosity, consistency, filtrate control, lubrication coefficient, among others. To be used as a component of the drilling fluids, the bentonite must be sodic, so that the necessary swelling for the application is achieved [12], since the set of viscosimetric and filtration parameters (apparent viscosity - AV, plastic viscosity - PV, and filtrate volume - FV) has great influence of the polycations in the liquid phase of dispersions [19]. For use as components of drilling fluids in water-based petroleum wells, the presence of sodium as the predominant cation is required. There are clays that are naturally sodic and swell in the presence of water, such as the North American bentonites of Wyoming, USA. In Boa Vista, Paraíba, Brazil, due to the disorderly extraction, the clays of the best mineralogical compositions are exhausted. The varieties commercialized today are predominantly polycationic, containing other clay minerals, such as illite and kaolinite, as well as considerable amounts of non-clay components such as quartz and feldspar, which in turn compromise their technological applications [3, 9-12]. The polycationic bentonite clays can be changed to sodic form by a reversible double-exchange chemical reaction using sodium carbonate (Na_2CO_3), since the interlamellar distance in the bentonites is higher when the lamellae have their charge compensated by the sodium ion, of lower valence, allowing the penetration of a greater amount of water in the space between the lamellae [1, 16, 17]. This explains why the expansion capacity of sodium bentonite is much higher than that of the calcium type [20]. The addition of Na_2CO_3 was made in the form of dry powder after its discovery in the 1930s, which presents as a serious drawback a low sodium diffusion coefficient in the clay structure due to the absence of water, and later in solution, because in the wet form there is, among other factors, a significant increase of this coefficient. After its addition, the additivated clay is submitted to a series of methods or processes called curing, whose objective is to optimize the cation exchange,

allowing greater efficiency of the reactions to obtain the clay in the sodic form, maximizing the development of specific properties, such as viscosity [19].

Over the years, many studies have emerged involving the process of additivation, strengthening the importance of its use for better rheological and filtration properties. In 1972, Zandonadi and Souza Santos [21] developed a large study on the transformation of polycationic bentonites into sodic and studied 18 different processes in ambient conditions, which resulted in the process 18, one of the most used to date for the conversion of polycationic bentonites into sodic. Brindley [22], Grim and Nüven [23], and Solano et al. [24, 25] studied drying temperatures to verify the eventual collapse of the galleries in bentonite clays before the addition of Na_2CO_3, in order to obtain better rheologies. It was confirmed that the presence of potassium makes difficult the exchange process after drying, obtaining a structure close to that of mica. New studies [10, 12, 20, 26] have been carried out in order to improve the various process variables for the optimization of the additivation process and its influence on the viscosity of dispersions of bentonite clays for aqueous drilling fluids. Although the literature presents such studies on the sodium adsorption process, in practice there is no uniformity on the influence of the Na_2CO_3 arrangement on the clay during the additivation process, and there is a need for studies that involve these process variables due to the large use of the additivation process in bentonite clays. In this way, this study aims to analyze the influence of the addition of Na_2CO_3 on the clay during the additivation process, the moisture content and cure time on the cation exchange and viscosity of bentonite clay dispersions for aqueous drilling fluids.

MATERIALS AND METHODOLOGY

Three bentonite clays were studied: AM1, AM2, and AM3, with dark brown, light brown, and reddish colors, respectively. AM1 was supplied by DBM Minerais, selected in the city of Olivedos, Paraíba, Brazil, and AM2 and AM3 were provided by Campos Novos Mine, Cubati, Paraíba, Brazil, belonging to the newly discovered deposits of bentonite clays. The bentonite clays were supplied in their natural form and subjected to a laboratory milling process and sieved (ABNT No. 200, 0.074 mm). For the process of additivation of bentonite clays, sodium carbonate (Na_2CO_3, Labsynth Prod. Lab., purity of 99.5%) was used. The clay samples were physically, chemically and mineralogically characterized through the techniques: chemical analysis by X-ray fluorescence (EDX 720, Shimadzu); granulometric analysis by laser diffraction (AG, 1064, Cilas); X-ray diffraction (XRD, XRD 6000, Shimadzu): with and without addition of ethylene glycol to confirm the clays of the smectite group; differential thermal analysis (DTA) and thermogravimetry (TG, RB-3000, BP Eng.): with a heating rate of 12.5 °C/min up to 1000 °C in air atmosphere and using calcinated aluminum oxide (Al_2O_3) as the reference sample in the DTA; and methylene blue adsorption method

[30] to determine cation exchange capacity (CEC) in meq/100 g of dry clay.

Two additivation processes of Na_2CO_3 were performed taking into account the moisture and CEC of the *in natura* bentonite clays: process 1 (P1) - Na_2CO_3 in solution: a concentrated aqueous solution of 2 N Na_2CO_3 (200 g Na_2CO_3/L) was mixed to 170 g of dry clay for each moisture content studied (25% to 60%); and process 2 (P2) - Na_2CO_3 powder: the mass of Na_2CO_3 powder added to each sample was calculated based on the sample mass used, 170 g (dry clay mass). The amount of Na_2CO_3 and water added to achieve moisture between

Table I - Amount of Na_2CO_3 and water added to each sample in the process 1.
[Tabela I - Quantidades de Na_2CO_3 e água adicionadas a cada amostra no processo 1.]

Sample	CEC[a] $\left(\dfrac{meq}{100\ g}\right)$	Na_2CO_3 volume[b] (mL)	Moisture content (%)	Water volume[c] (mL)
AM1 and AM3	72	32.44	25	*
			35	10.06
			45	27.06
			50	35.56
			60	52.56
AM2	74	33.34	25	*
			35	9.16
			45	26.16
			50	34.66
			60	51.66

[a] *cation exchange capacity;* [b] *Na_2CO_3 in solution;* [c] *added to achieve required moisture;* * correction made in the dry oven at 60 °C.

Table II - Amount of Na_2CO_3 and water added to each sample in the process 2.
[Tabela II - Quantidades de Na_2CO_3 e água adicionadas a cada amostra no processo 2.]

Sample	CEC[a] $\left(\dfrac{meq}{100\ g}\right)$	Na_2CO_3 mass[b] (g)	Moisture content (%)	Water volume[c] (mL)
AM1 and AM3	72	6.49	25	25.50
			35	42.50
			45	59.50
			50	68.00
			60	85.00
AM2	74	6.67	25	25.50
			35	42.50
			45	59.50
			50	68.00
			60	85.00

[a] *cation exchange capacity;* [b] *Na_2CO_3 powder;* [c] *added to achieve required moisture.*

25% and 60% (dry base) to each sample are given in Tables I and II for the processes 1 and 2, respectively. Subsequently, the samples were placed in hermetically sealed plastic bags during the cure times of 7, 15, 30 and 45 days.

Preparation and characterization of the dispersions: after the curing period, the apparent viscosity (AV), plastic viscosity (PV), and filtrate volume (FV) of the samples were determined. The polycationic and monocationic bentonite dispersions were prepared at the concentration specified in the Petrobras standard [27], 24.3 g/500 mL of deionized water (4.86% by mass), then homogenized with an agitator (500 W, Marconi) at approximately 15000 rpm for 20 min, shortly after resting for 24 h. The parameters AV and PV were measured using a viscometer (35A, Fann) according to AV=L600/2 and PV=L600-L300, in cP (equivalent to mPa.s). FV was determined by a filter press test, in which the dispersion was inserted and the filtrate collected over a period of 30 min after the application of a pressure of 690±35 kPa (100±5 psi).

RESULTS AND DISCUSSION

Table III shows the results of the chemical composition of the samples. It was observed that: SiO_2 contents in the range of 48% to 54% and Al_2O_3 contents between 21% and 23%, from the tetrahedral and octahedral sheets within the clay and other non-clay minerals; 8%-12% of Fe_2O_3 and 2%-3% of MgO, resulting from isomorphic substitutions occurring in the octahedral sheet and other non-clay minerals; 0.5%-1.4% of CaO and 0.9%-1.0% of TiO_2, among other oxides. These results are typical of the clays of the State of Paraíba, Brazil [12, 20, 26, 28-30].

Table IV shows the results of the granulometric distribution of the samples. It was observed the highest fraction of accumulated volume with a diameter of less than 2 µm (83.33%) for the sample AM1 and fractions of 55.97% and 56.70% for the samples AM2 and AM3, probably related to the concentrations of clay fraction resulting from the purification process [26]. The AM1 sample had the smallest diameter at 50% of 0.53 µm and an average diameter of 1.09 µm; the samples AM2 and AM3 presented diameters at 50% of 1.68 and 1.67 µm, respectively, and an average diameter of 2.67 and 2.32 µm, respectively. These values can be related to the amount of non-clay materials present in the samples and can be correlated with the results of chemical composition (Table III). These results corroborated those presented in [12, 20, 26]. The results of the AM1 sample may lead to better viscosimetric properties, according to Gaidzinski et al. [31, 32], who state that better viscosimetric properties are found in the samples with smaller average diameters and higher particle contents with x<2 µm.

Fig. 1 shows the XRD patterns of the samples AM1, AM2, and AM3 with and without ethylene glycol. It were observed the following mineralogical phases: montmorillonite (JCPDS 10-0357), characterized by interplanar distances (d_{hkl}) of 15.60, 4.46, 3.57, and 2.56 Å, which was confirmed by the use of ethylene glycol,

Table III - Chemical composition (wt%) of AM1, AM2, and AM3 samples.
[Tabela III - Composição química (% em massa) das amostras AM1, AM2 e AM3.]

Sample	SiO$_2$	Al$_2$O$_3$	MgO	Fe$_2$O$_3$	CaO	TiO$_2$	Others	LOI
AM1	54.53	21.03	2.57	9.75	0.73	0.93	0.43	9.50
AM2	48.20	23.04	3.09	8.25	1.39	1.01	0.97	14.14
AM3	48.89	22.26	3.08	12.79	0.48	0.97	2.34	9.19

LOI - loss on ignition.

Table IV - Granulometric distribution data by laser diffraction of the samples.
[Tabela IV - Dados de distribuição granulométrica por difração a laser das amostras.]

Sample	D<2 μm (%)	Diameter at 50% (μm)	Average diameter (μm)
AM1	83.33	0.53	1.09
AM2	55.97	1.68	2.67
AM3	56.70	1.67	2.32

increasing the interplanar distance from 15.60 to 17.48 Å; kaolinite (JCPDS 78-2110) characterized by d$_{hkl}$ of 7.16 and 2.55 Å; and quartz (JCPDS 46-1045) characterized by d$_{hkl}$ of 4.25 and 3.34 Å. The red patterns indicated the characteristic peak of the montmorillonite with the addition of ethylene glycol, confirming that the samples were, in fact, bentonite clays. In general, the X-ray diffraction patterns confirmed qualitatively that the clays presented typical patterns of the bentonite clays with other non-clay minerals, similar to other studies [12, 20, 26, 29, 30, 33].

Fig. 2 shows the DTA and TG results of the samples. Analyzing the DTA curves (Fig. 2a), the following thermal transformations were observed for the samples AM1, AM2 and AM3, respectively: an endothermic peak at approximately 141, 73 and 72 °C, characterizing the presence of water (free and adsorbed) and an exothermic band indicating probably the presence of organic matter in the samples AM1 and AM2; afterward, the curves showed an endothermic peak at around 558, 495 and 494 °C, which characterized the presence of hydroxyls of smectite and kaolinite, thus confirming the presence of these minerals in accordance with the results of chemical composition (Table III) and granulometric analysis (Table IV); and an exothermic peak at approximately 918, 922 and 921 °C, related to the nucleation of the mullite with release of β-quartz. Based on TG curves (Fig. 2b), it was observed total mass losses of approximately 20.5%, 23,0% and 21.3%, related to the losses of water (free, adsorbed and coordinated) and hydroxyls for the samples AM1, AM2, and AM3, respectively. It was verified that the studied samples presented similar thermal behavior to the bentonite clays of the State of Paraíba, corroborating the results of other studies [9, 12, 20, 28, 30, 34-36].

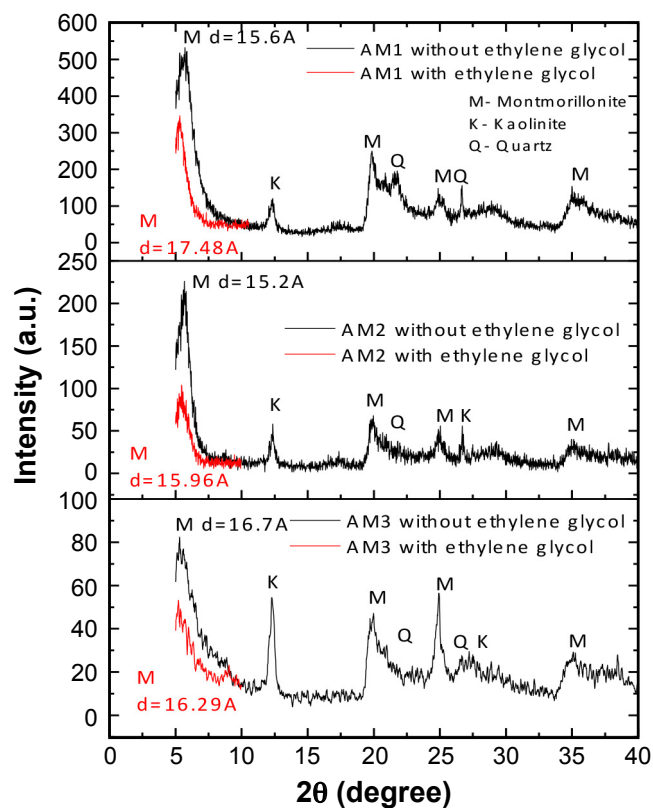Table V shows the results of CEC, AV, PV, and FV of the

Figure 1: XRD patterns of samples AM1, AM2, and AM3 with and without ethylene glycol.
[Figura 1: Padrões de DRX das amostras AM1, AM2 e AM3 com e sem etileno glicol.]

in natura samples, that is, before the additivation process, based on the Petrobras standard [27]. It was observed that the viscosimetric and filtration properties of the *in natura* samples (AM1, AM2, and AM3) did not meet the requirements established by the standard [27], since polycationic clays need to have their cations exchanged for sodium (Na$^+$) to be more strongly hydrated, exhibiting more significant swelling of the particles, thus causing an increase in their viscosities and a decrease in the filtrate volume [20, 37].

Fig. 3 shows the results of CEC for processes 1 and 2 with the moisture contents of 25% to 60% and the cure times of 7 to 45 days for the samples AM1, AM2, and AM3. It was observed the increase of CEC from 7 to 15 days of cure in both processes (1 and 2), showing that the optimal cure time for the samples was 15 days; after that, the values of CEC decreased progressively as the time of cure increased,
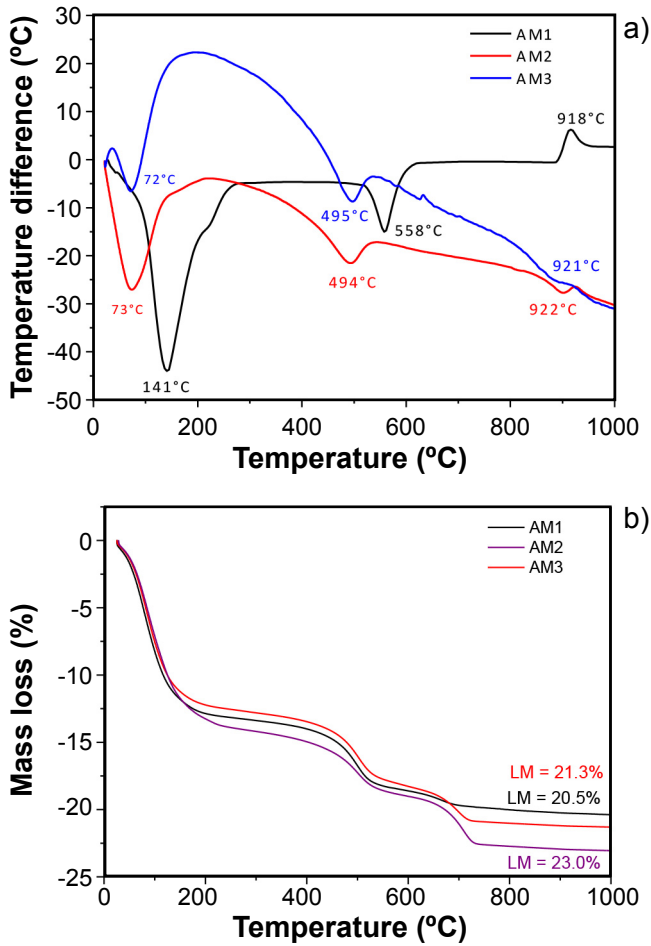
Figure 2: DTA (a) and TG (b) curves of the samples AM1, AM2, and AM3.
[Figura 2: Curvas de DTA (a) e TG (b) das amostras AM1, AM2 e AM3.]

Table V - Apparent viscosity (AV), plastic viscosity (PV), and filtrate volume (FV) of the *in natura* samples.
[Tabela V - Viscosidade aparente (AV), viscosidade plástica (PV) e volume de filtrado (FV) das amostras in natura.]

Sample	Moisture content (%)	CEC[a] ($\frac{meq}{100\ g}$)	AV (cP)	PV (cP)	FV (mL)
AM1	10.0	72	11.0	3.0	17.0
AM2	10.0	74	12.0	2.5	16.5
AM3	10.0	72	13.0	2.0	17.0
Specif.[b]	*	*	>15.0	>4.0	<18.0

[a] cation exchange capacity; [b] Petrobras specification [27]; * value not specified.

probably due to a reversal of the cation exchange reactions, causing consequently the loss of properties against the most diverse important data on the lifetime or validity of these industrial inputs [20, 26]. The moisture contents of 50% and 60% led to higher CEC values between 83 and 94 meq/100 g, probably due to the fact that at these levels the amount of Na_2CO_3 used was higher, based on the mass
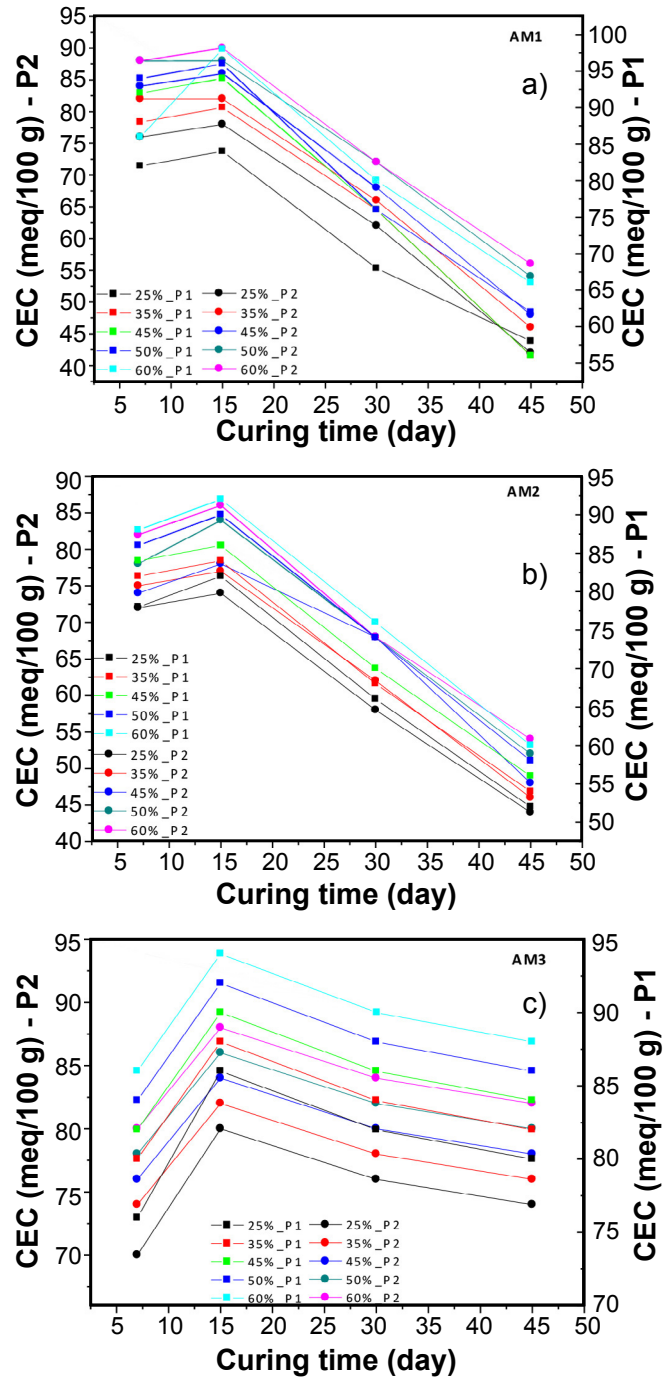

Figure 3: CEC of the samples AM1 (a), AM2 (b), and AM3 (c) for the processes 1 (P1) and 2 (P2) with the moisture contents of 25% to 60% as a function of cure time.
[Figura 3: CTC das amostras AM1 (a), AM2 (b) e AM3 (c) para os processos 1 (P1) e 2 (P2) nos teores de umidades de 25% a 60% em função do tempo de cura.]

of dry clay and CEC of the clay *in natura*, being able to allow a greater basal spacing by the greater amount of Na+, also allowing the penetration of a greater amount of water in the space between the lamellae and a greater adsorption of molecules of methylene blue, also explaining the cause of the increase of the CEC of the additivated samples with respect to their *in natura* state [10, 12, 26, 29, 30]. Comparing the

Table VI - Apparent viscosity (AV), plastic viscosity (PV), and filtrate volume (FV) of the additivated samples by processes 1 (P1) and 2 (P2).
[Tabela VI - Viscosidade aparente (AV), viscosidade plástica (PV) e volume de filtrado (FV) das amostras aditivadas pelos processos 1 (P1) e 2 (P2).]

Sample	Moisture content (%)	Cure time (day)	AV (cP)	PV (cP)	FV (mL)
AM1-P1	50	15	26.0	8.0	9.0
AM1-P1	60	15	27.0	9.0	11.0
AM1-P2	50	15	23.5	6.0	11.0
AM1-P2	60	15	24.0	7.0	13.0
AM2-P1	50	15	25.0	10.0	7.0
AM2-P1	60	15	26.0	10.0	9.0
AM2-P2	50	15	22.5	6.0	7.0
AM2-P2	60	15	23.0	7.0	11.0
AM3-P1	50	15	25.0	8,5	6.0
AM3-P1	60	15	26.0	9.0	7.0
AM3-P2	50	15	23.0	7.0	7.0
AM3-P2	60	15	24.0	8.0	8.0
Specif.[a]	-*	-*	>15.0	>4.0	<18.0

[a] Petrobras specification [27]; * value not specified.

two processes of additivation (1 and 2), it was verified that the best results were found for process 1, probably due to the increase of the contact surface of the solution with the sample [38], since it favored the cation exchange, although process 2, which used powdered Na_2CO_3, is the most used in the industries. Furthermore, probably sodium by increasing basal spacing may be allowing for greater adsorption of methylene blue molecules, varying the CEC according to the procedure used. Thus, process 1 tended to improve the kinetics of the reaction between Na_2CO_3 and the clays, resulting in an increase in CEC values [20, 26]. In general, the influences of Na_2CO_3 in the samples, moisture content (Na_2CO_3 concentration), and cure time in the CEC of the samples were observed, and it was, therefore, necessary to analyze the viscosity and filtration properties of the dispersions obtained.

Table VI shows the results of viscosity (AV, PV) and filtration (FV) of the samples after the additivation processes 1 and 2, from the samples with the best CEC results obtained with the moisture contents of 50% and 60% and the cure time of 15 days (Fig. 3), based on the Petrobras standard [27]. It was seen that the AM1 sample presented relatively better AV results than AM2 and AM3, probably due to the higher fraction of D<2 μm particles (Table IV) and the lower amount of the kaolinite phase (Fig. 1). For the two additivation processes (Table VI), there was an improvement in the results of AV, PV, and FV, when compared to the results before the additivation (Table V), since the clays

when sodic are more heavily hydrated, presenting more significant swelling of the particles, causing an increase in viscosity values [20, 26]. It was also observed that, after the additivation by both processes (1 and 2), the sample dispersions presented results of AV, PV, and FV that reached the specifications [27, 37]. The results also showed that the reversibility of the reactions could be verified directly by the viscosimetric properties of the hydro-reactive fluids [26]. Comparing the two additivation processes, better viscosity and filtration results were found for process 1, because this process also influenced the CEC with better results (Fig. 3), as it provided the highest cation exchange between Na_2CO_3 and the clays, resulting in an increase in CEC values, and consequently in AV and PV, and a decrease in FV, which was reinforced by the optimum cure time and moisture increase [20, 26, 37-41], since the exchangeable ions strongly influence the physicochemical and viscosimetric properties of bentonite clays and their dispersions [20, 26].

CONCLUSIONS

It could be concluded that the additivation process influenced the cation exchange capacity (CEC) of additivated bentonite clays and, consequently, the viscosimetric and filtration properties. Additivation with sodium carbonate in aqueous solution was more effective than using sodium carbonate in powder form. It was also concluded that high moisture content (50% and 60%) and optimum cure time (15 days) can increase CEC, apparent viscosity (AV), and plastic viscosity (PV) and decrease filtrate volume (FV), but if the cure time is exceeded, these parameters can be negatively affected for some industrial applications, such as water drilling fluids. The studied bentonite clays additivated by the two processes reached the current industrial specifications and can be applied to water drilling fluids.

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