Influence of MgO and $CaCl_2$ on the rheological properties of bentonitic clays from the new Paraíba-Brazil deposits using experimental planning and statistical analysis

(Influência do MgO e $CaCl_2$ nas propriedades reológicas de argilas bentoníticas dos novos depósitos da Paraíba-Brasil utilizando planejamento experimental e análise estatística)

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Abstract

New deposits of bentonite clays have been discovered in the Brazilian State of Paraíba; the most recent was at the municipality of Olivedos. Recent studies have discovered the presence of high levels of non-clay minerals that can produce unsatisfactory results when attempting to use these clays in drilling fluids. In order to make them suitable for this purpose, the MgO and $CaCl_2$ as chemical additives were used and their influences on the rheological properties of these clays were analyzed, using an experimental planning technique and statistical analysis. The samples were obtained using experimental modeling by the delineation of mixtures technique; first, the clays were transformed with sodium carbonate and then dosed with MgO and $CaCl_2$. The rheological properties, apparent viscosity (AV) and plastic viscosity (PV) were determined according to the Petrobras standard (AV≥15 cP; PV≥4 cP). The results showed that the values of AV and PV increased considerably and that MgO was the additive that contributed most to the improvement of these properties, making these additives suitable for use in water-based drilling fluids.

Keywords: Olivedos' bentonites, additives, drilling fluids.

Resumo

Novos depósitos de argila bentonítica foram descobertos no estado brasileiro da Paraíba, sendo o mais recente no município de Olivedos. Estudos recentes descobriram a presença de altos níveis de minerais não argilosos que podem produzir resultados insatisfatórios ao tentar usar essas argilas em fluidos de perfuração. Para torná-los adequados para esse fim, utilizaram-se MgO e $CaCl_2$ como aditivos químicos e analisaram-se suas influências nas propriedades reológicas dessas argilas, utilizando técnica de planejamento experimental e análise estatística. As amostras foram obtidas utilizando modelagem experimental pela técnica de delineamento de misturas; inicialmente as argilas foram transformadas com compostos de sódio e posteriormente dosadas com MgO e $CaCl_2$. As propriedades reológicas, viscosidade aparente (AV) e viscosidade plástica (PV), foram determinadas de acordo com a normativa da Petrobras (AV≥15 cP; PV≥4 cP). Os resultados mostraram que os valores de AV e PV aumentaram consideravelmente e que o MgO foi o aditivo que mais contribuiu para a melhoria dessas propriedades, tornando-os adequados para uso em fluidos de perfuração à base de água.

***Palavras-chave**: bentonitas de Olivedos, aditivos, fluidos de perfuração.*

INTRODUCTION

Paraíba is the Brazilian State containing several bentonite clay deposits, mainly in the Boa Vista municipality. These deposits have already reached the exhaustion phase. Recent studies [1-4] have been developed using bentonites from newly discovered deposits at the Olivedos, Cubati, Pedra Lavrada, and Sossego municipalities, but the presence of non-clay minerals such as mica and quartz render them unsuitable for use in drilling fluids. Because of this difficulty, several companies in Paraíba have begun to import bentonitic clays from countries such as Turkey and India, in order to preserve the continuity of their production processes. A viable alternative to using these Paraíba's clays is to treat them with sodium carbonate (Na_2CO_3) isolated or combined with secondary chemical additives to find intermediate gels between the flocculation and deflocculation states that characterize water-based drilling fluids.

According to van Olphen [5], drilling fluids are clay-water systems having an intermediate behavior between

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flocculated and deflocculated state, which are obtained naturally from Wyoming sodium clays that provide the apparent and plastic viscosities originally used by API (American Petroleum Institute) as a worldwide standard. The deflocculated systems have high apparent and plastic viscosities (AV and PV), whereas the flocculated systems can be divided into two types: 1) flocculated gel (as termed in [5]) with high apparent viscosity and low plastic viscosity, having anisometric clay particles forming a 'face to edge' house of cards micro-configuration; and 2) flocculated with phase separation, where the anisometric clay particles have a 'face to face' micro-configuration. In these extreme cases, secondary additives (also called chemical additives) can be used to transform this clay-water system into a true drilling fluid suitable for the specific geological conditions found at each drilling site, and is a vast and complex subject covered by thousands of patents and industrial secrets.

Several studies [6-11] have demonstrated that the use of ions, such as Ca^{2+}, Mg^{2+}, K^{+}, or Li^{2+} as secondary chemical additives in clay-water systems, can transform them in systems ranging from flocculated to deflocculated, according to the proportion and combination of ions added. These systems have been shown to have satisfactory rheological property values at intermediate points, where traditional techniques do not indicate adequate results. Some researchers [12-14] have used statistical and mathematical techniques to study the effect of clay compositions and additives on the rheological properties of clay-water systems. This methodology has found application in a number of technological areas [13-17]. In the cases mentioned, this methodology led to better results and optimized the systems with a minimum of experiments. However, there is a lack of knowledge regarding the use of these systems with clays from the newly discovered deposits mentioned above. In order to improve the rheological behavior of the new bentonite deposits in the Paraíba State, Brazil, that contain a high amount of non-clay minerals leading to unsatisfactory results using traditional tests and the Petrobras standard [18], in this study $CaCl_2$ and MgO flocculants were investigated as secondary chemical additives to make possible the use of the new Olivedos-Paraíba clays in water-based drilling fluids using the mixture delineation technique and statistical analysis.

MATERIALS AND METHODS

The clays studied, named AM1 and AM2, were obtained from samples of the new deposits in the Olivedos municipality, Paraíba-Brazil, and the average samples were obtained using the delineation of mixture experiment modeling technique [13]. Among the samples studied in [19], those from the Olivedos municipality showed the most promising results when mixed with Chocolate clay from the Boa Vista municipality. In this study, Olivedos clays were also investigated individually, which did not produce satisfactory results, driving the decision to use secondary additives with these samples. The physical, chemical and mineralogical characterizations of the used clay samples are described in [12], which shows that they had clay minerals from the smectite group with kaolinite and mica, and quartz as a non-clay mineral. These clays were transformed with a sodium compound through the classic process with the addition of sodium carbonate at a ratio of 125 meq/100 g of dry clay. The results of the rheological tests, according to the Petrobras standard [18], were unsatisfactory. The following compounds were used as additives: sodium carbonate (Na_2CO_3, Vetec); 99.0% pure calcium chloride ($CaCl_2$); and 99.0% pure magnesium oxide (MgO), both supplied by Casa da Química.

The clays were dried in an oven at approximately 60 °C, fragmented in a ball mill and sieved with an ABNT No. 200 (0.074 mm) sieve. After processing, the polycationic natural clays were transformed with sodium carbonate as described above and then cured for a period of 5 days to allow a complete exchange of cations. Following this, MgO and $CaCl_2$ were added using the delineation of the mixture experiment modeling technique [20]. The dispersions were prepared and AV and PV parameters were determined according to Petrobras standard [18]. To define the compositions, simplex centroid network planning {3,2} was used, with interior points added, totaling ten experimental runs. These experiments were performed randomly and each test was conducted in duplicate. The proportions of the components ranged from 97.5% to 100% for clay and from 0% to 2.5% for MgO and $CaCl_2$. The compositions are shown in Table I. The results were obtained in duplicate and the statistical analysis was performed with Statistica v.6.0 software.

RESULTS AND DISCUSSION

Table II shows the results of rheological parameters obtained for the dispersions prepared with the compositions listed in Table I. From the results obtained, including duplicates, regression equations were generated (Table

Table I - Proportions of components (%) of simplex centroid network planning {3,2} with interior points added.
[Tabela I - Proporções dos componentes (%) do planejamento em rede simplex centroide {3,2} aumentado com pontos interiores.]

Composition	Clay (AM_1 or AM_2)	MgO	$CaCl_2$
1	100.00	0.00	0.00
2	97.50	2.50	0.00
3	97.50	0.00	2.50
4	98.75	1.25	0.00
5	98.75	0.00	1.25
6	97.50	1.25	1.25
7	99.16	0.42	0.42
8	97.91	1.67	0.42
9	97.91	0.42	1.67
10	98.34	0.83	0.83

Table II - Rheological parameters of the compositions studied.
[Tabela II - Parâmetros reológicos das composições estudadas.]

Composition	AV_1 (cP)	PV_1 (cP)	AV_2 (cP)	PV_2 (cP)
1	19.75	1.00	13.50	3.00
	17.00	2.00	12.00	3.00
2	17.50	7.00	27.50	6.00
	20.00	6.00	26.00	7.00
3	11.00	4.00	17.00	4.00
	11.50	4.00	17.00	5.00
4	19.00	4.00	24.50	5.00
	18.00	4.00	22.50	4.00
5	11.00	3.00	14.00	3.00
	10.00	4.00	13.00	3.00
6	17.50	6.00	31.50	9.00
	18.00	5.00	29.50	8.00
7	20.00	4.00	22.00	4.00
	20.00	3.00	24.00	4.00
8	17.50	3.00	20.00	5.00
	20.50	5.00	22.00	4.00
9	13.00	5.00	18.00	4.00
	15.50	4.00	18.50	4.00
10	20.00	5.00	26.50	6.00
	20.00	6.00	24.50	5.00
Specification EP-1EP-00011-A (19) API 13A: $AV \geq 15cP$; $PV \geq 4cP$				

AV_1 and PV_1 - AV (apparent viscosity) and PV (plastic viscosity) for compositions formulated with sample AM_1; AV_2 and PV_2 - AV and PV for compositions formulated with sample AM_2.

Table III - Decoded regression equations for AV_1, PV_1, AV_2, and PV_2.
[Tabela III - Equações de regressão decodificadas para AV_1, PV_1, AV_2 e PV_2.]

Variable	Equation
AV_1	$AV_1=0.19.AM_1–0.04.B+138.91.C–1.46.AM_1.C+0.03.AM_1.B.C$
PV_1	$PV_1=0.02.AM_1+1.69.B+1.02.C$
AV_2	$AV_2=0.1.AM_2+134160.3.B+1.6.C–2039.0.AM_2.B–675.1.B.C+7.0.AM_2.B.(AM_2-B)$
PV_2	$PV_2=0.03.AM_2+1.33.B+0.53.C+1.54.B.C$

AM_1, AM_2, B, and C represent clay AM_1, clay AM_2, MgO, and $CaCl_2$, respectively.

Table IV - Statistical parameters of the analyses of variance for the AV and PV variables relative to the selected models.
[Tabela IV - Parâmetros estatísticos das análises de variância das variáveis viscosidade aparente (AV) e viscosidade plástica (PV) relativos aos modelos escolhidos.]

Variable	Model	Test F_{cal}	F_{cal}/F_{tab}	p-value	R^2
AV_1	Special cubic	21.0972	6.8945	0.0000	0.8491
PV_1	Linear	16.7879	4.6762	0.0001	0.6639
AV_2	Complete cubic	35.3216	11.9330	0.0000	0.9266
PV_2	Quadratic	12.8902	3.9784	0.0002	0.7073

F_{cal} - calculated F-test (Fisher test); F_{cal}/F_{tab} - ratio between the calculated F-test and the tabulated F-test; p-value - descriptive level or probability of significance; R^2 - correlation coefficient.

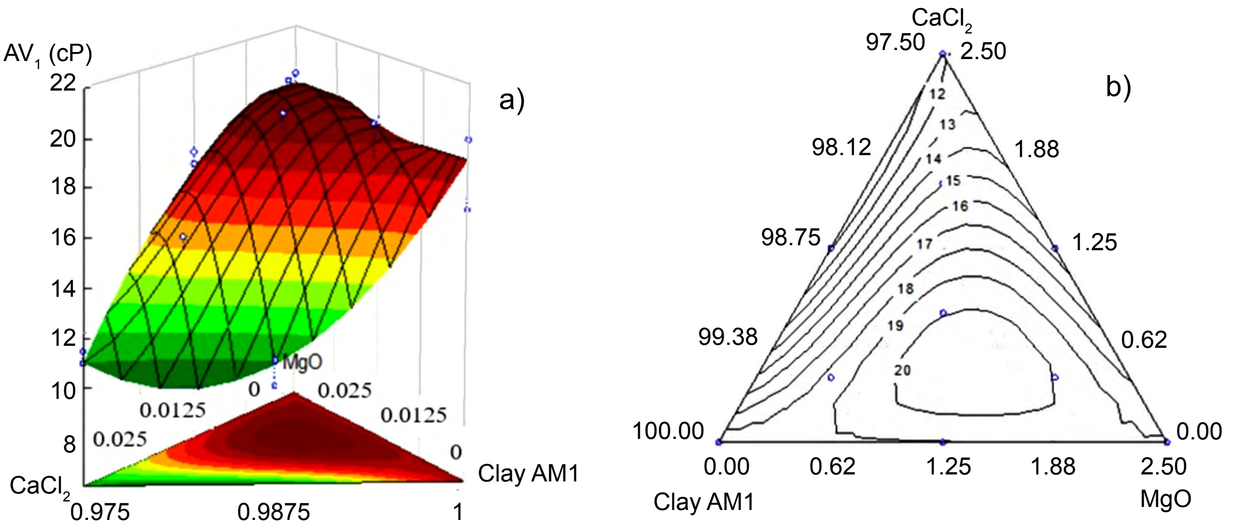

Figure 1: Response surface (a) and contour plot (b) for AV_1 calculated from the special cubic model as a function of the quantity of AM_1 clay, MgO, and $CaCl_2$.

[Figura 1: Superfície de resposta (a) e curvas de nível (b) para AV_1 *calculadas a partir do modelo cúbico especial em função da quantidade da argila* AM_1*, MgO e* $CaCl_2$*.]*

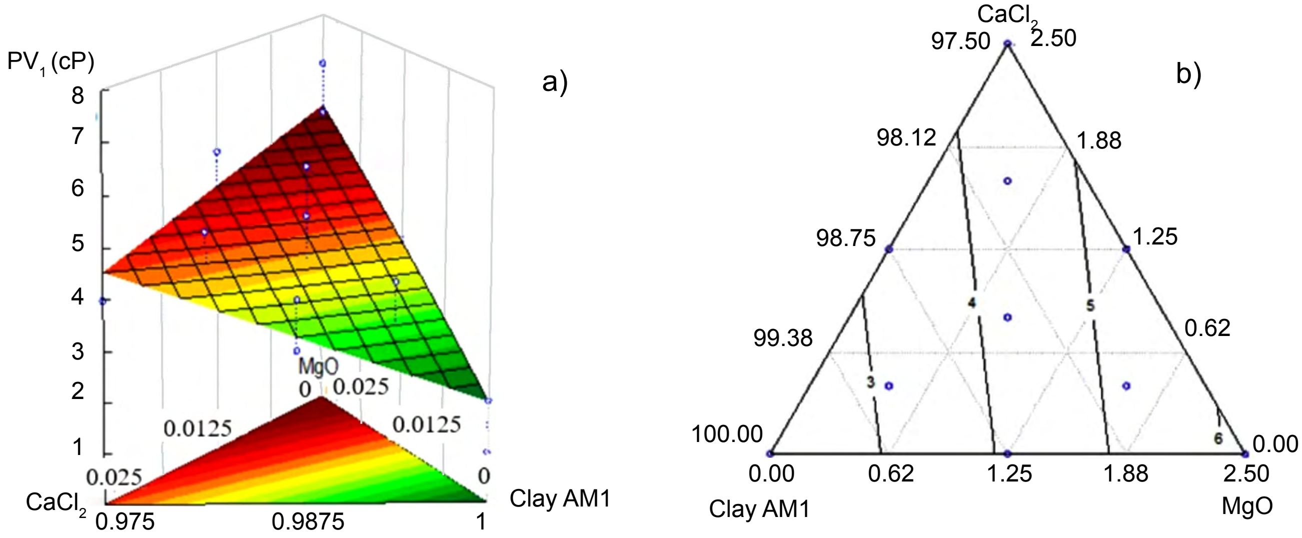

Figure 2: Response surface (a) and contour plot (b) for PV_1 calculated from the linear model as a function of the quantity of AM_1 clay, MgO, and $CaCl_2$.

[Figura 2: Superfície de resposta (a) e curvas de nível (b) para PV_1 *calculadas a partir do modelo linear em função da quantidade da argila* AM_1*, MgO e* $CaCl_2$*.]*

III), correlating the mass proportion of clay and MgO and $CaCl_2$ additives with the apparent viscosity (AV) and plastic viscosity (PV). The equations presented were statistically significant at the 95% confidence level and described the behavior of the dispersions' properties as a function of the component proportions. Table IV presents the main statistical parameters obtained from the analysis of variance of the models presented in Table III. The statistical parameters indicated that the models were well-adjusted. The p-values showed that the models were statistically significant at the stipulated level (p-value ≤ level of significance). The relationships between the calculated and tabulated F-test values for AV_1, PV_1, and AV_2 showed that the models were not only significant but also predictive. For PV_2, it can be stated that the model was significant [14, 21].

Figs. 1 and 2 illustrate the response surfaces and contour plots for AV_1 and PV_1 values, respectively. It was observed that MgO, as $Mg(OH)_2$, was the component that most contributed to the increase of AV, probably because the Mg^{2+} cation acted as a bridging bond that brought the clay particles closer together, leading to a greater tendency to flocculate. This ion, even when hydrated, decreases the thickness of the adsorbed water layer due to its higher charge and smaller ionic radius [7, 14] that approximated the clay particles

According to Sousa Santos [21], the addition of bivalent cations decreases the electrokinetic potential of

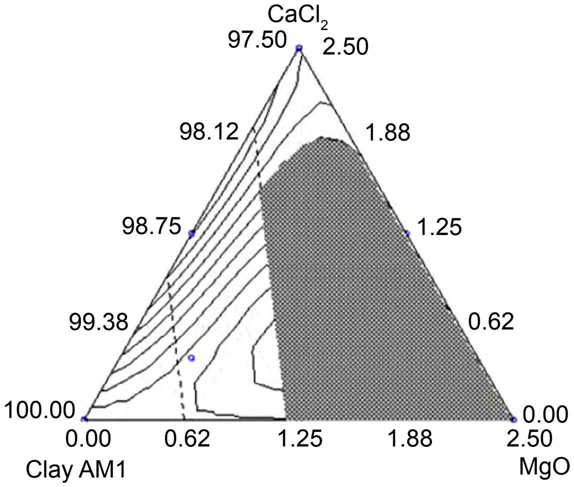

Figure 3: Intersection between the AV_1 and PV_1 contour plots showing a cross-sectional area of compositions with $AV_1 \geqslant 15.0$ cP and $PV_1 \geqslant 4.0$ cP.
[Figura 3: Intersecção das curvas de níveis de AV_1 e PV_1 apresentando área hachurada de composições com $AV_1 \geqslant 15,0$ cP e $PV_1 \geqslant 4,0$ cP.]

the clay particles and, therefore, the repulsion between these particles. As a consequence, particle agglomerates are formed, that is, the phenomenon of flocculation occurs. Polyvalent cations replace sodium on the surface of the clay particles, reducing and reversing their surface charge. After this reduction and that of the electrokinetic potential, the particles naturally associate 'face to face', producing the flocculated state with phase separation. The response surfaces for PV make it possible to conclude that, although both additives contributed to the increase of the plastic viscosity, MgO as $Mg(OH)_2$ was the component that more effectively increased this parameter. MgO in the $Mg(OH)_2$ form induced face-to-face interactions, resulting in the flocculated state, which favored both apparent viscosity (AV) and plastic viscosity (PV). In the flocculated gel state, it has high AV and low PV [7, 14].

Fig. 3 shows the overlapping between the contour plots of parameters AV_1 and PV_1. The cross-hatched area indicated the compositions whose rheological

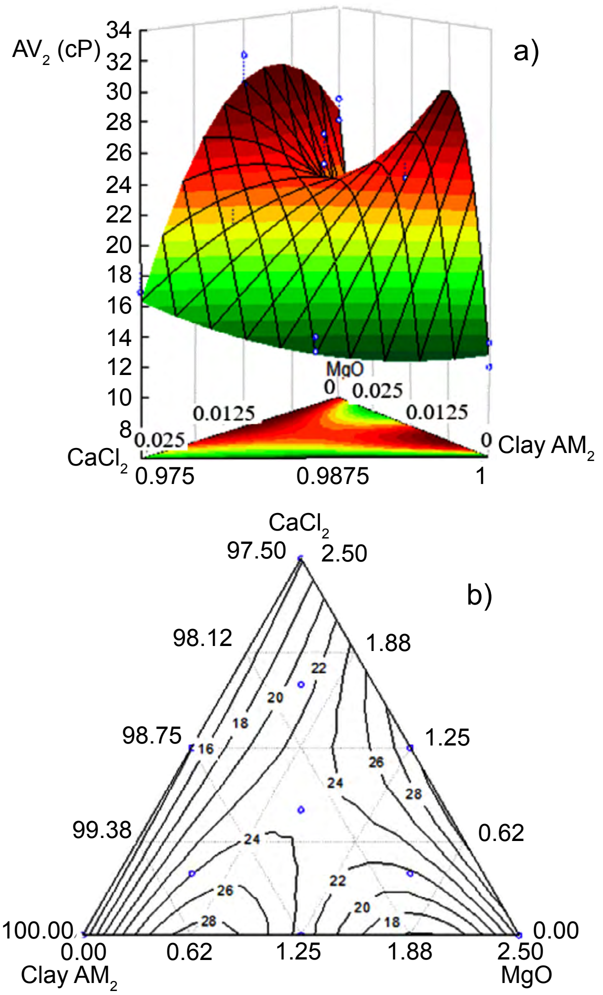

Figure 4: Response surface (a) and contour plot (b) for AV_2 calculated from the complete cubic model as a function of the amount of clay AM_2, MgO, and $CaCl_2$.
[Figura 4: Superfície de resposta (a) e curvas de nível (b) para AV_2 calculadas a partir do modelo cúbico completo em função da quantidade da argila AM_2, MgO e $CaCl_2$.]

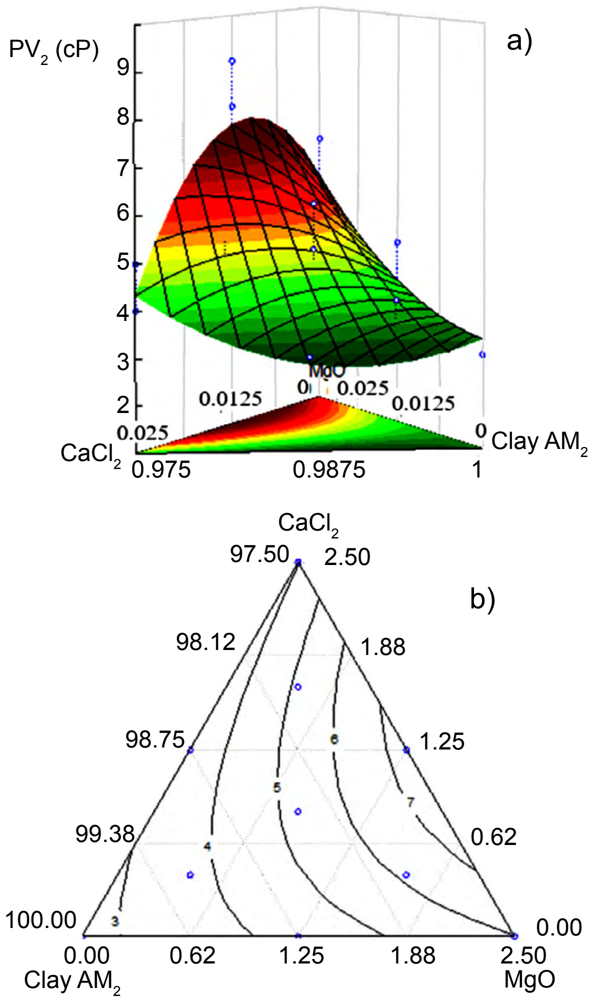

Figure 5: Response surface (a) and contour plot (b) for PV_2 calculated from the quadratic model as a function of the amount of clay AM_2, MgO, and $CaCl_2$.
[Figura 5: Superfície de resposta (a) e curvas de nível (b) para PV_2 calculadas a partir do modelo quadrático em função da quantidade da argila AM_2, MgO e $CaCl_2$.]

parameters AV_1 and PV_1 met the requirements established by the Petrobras standard [18] for use as drilling fluids in water-based oil wells [14]. In order to validate the model experimentally, compositions within the limits were selected. Using the equations from Table III, the predicted values for AV_1 and PV_1 were calculated and then determined experimentally [14]. The results are shown in Table V. The predicted and experimentally-measured results for the AV_1 and PV_1 values were similar, making it possible to state that the statistical models were reliable for predictive purposes. Similar results were obtained in [13].

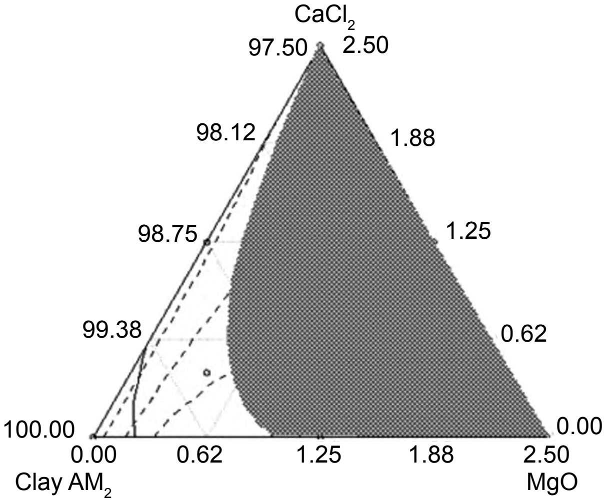

Figure 6: Intersection between the AV_2 and PV_2 contour plots showing a cross-sectional area of compositions with $AV_2 \geq 15.0$ cP and $PV_2 \geq 4.0$ cP.

[Figura 6: Intersecção das curvas de níveis de AV_2 e PV_2 apresentando área hachurada de composições com $VA_2 \geq 15,0$ cP e $VP_2 \geq 4,0$ cP.]

Figs. 4 and 5 illustrate the response surfaces and contour plots for AV_2 and PV_2, respectively. The addition of MgO and $CaCl_2$ improved AV and PV over most of the composition region and contributed to their increase. Fig. 6 shows the overlap between the contour plots of parameters AV_2 and PV_2. The cross-hatched area indicated the compositions whose rheological parameters met the requirements established by the Petrobras standard [18] for use in water-based oil well drilling fluids. In order to experimentally validate the model, compositions within the determined limits were selected. Using the equations from Table III, the predicted values for AV_2 and PV_2 were calculated and then determined experimentally. The results are shown in Table VI. The predicted and experimentally-measured results for the values of AV_2 and PV_2 make it possible to conclude that the statistical models were reliable for predictive purposes. Similar results were obtained in [13].

CONCLUSIONS

It was possible to conclude that the use of secondary additives MgO and $CaCl_2$ increased the apparent and plastic viscosity values of dispersions prepared with smectite clays from the Olivedos municipality, Paraíba State, Brazil. The results also showed that after the additivation process the clays studied became suitable for use in water-based drilling fluids and that the experimental planning technique proved to be an important and fundamental tool in the study of the optimization and modeling of clay compositions, avoiding the need to import raw materials for the extraction of petroleum in Brazil.

Table V - Predicted and experimentally measured values for rheological parameters AV_1 and PV_1.

[Tabela V - Valores preditos e medidos experimentalmente para os parâmetros reológicos AV_1 e PV_1.]

Composition	Component proportion (%)			Predicted value		Experimental value	
	AM_1	MgO	$CaCl_2$	AV_1 (cP)	PV_1 (cP)	AV_1 (cP)	PV_1 (cP)
i	97.70	2.10	0.20	19.18	5.73	19.12	6.35
ii	97.74	0.79	1.47	16.40	4.81	17.85	4.25
iii	99.52	0.28	0.20	18.16	2.69	18.83	3.79
iv	98.30	0.95	0.75	20.39	4.36	19.03	4.58

Table VI - Compositions used for the model tests and the predicted and experimentally measured values for rheological parameters AV_2 and PV_2.

[Tabela VI - Composições utilizadas nos testes dos modelos e os respectivos valores observados e previstos de AV_2 e PV_2.]

Composition	Component proportion (%)			Predicted value		Experimental value	
	AM_2	MgO	$CaCl_2$	AV_2 (cP)	PV_2 (cP)	AV_2 (cP)	PV_2 (cP)
i	98.73	0.95	0.32	24.92	4.57	25.50	5.00
ii	98.14	.95	0.91	23.79	5.74	23.50	5.00
iii	97.74	1.94	0.32	22.88	6.35	22.50	6.00
iv	97.70	0.36	1.94	20.84	5.22	21.50	5.50

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