Influence of MgO and CaCl₂ on the rheological properties of bentonitic clays from the new Paraíba-Brazil deposits using experimental planning and statistical analysis

(Influência do MgO e CaCl₂ 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 CaCl₂ 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 CaCl₂. 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 CaCl₂ 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 CaCl₂. 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 (Na₂CO₃) 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
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], were unsatisfactory. The following compounds were used as additives: sodium carbonate (Na\(_2\)CO\(_3\), 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 I - Proportions of components (%) of simplex centroid network planning \{3,2\} with interior points added).

![Table I](image-url)

**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 minerals. 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 compounded were used as additives: sodium carbonate (Na\(_2\)CO\(_3\), Vetec); 99.0% pure calcium chloride (CaCl\(_2\)); and 99.0% pure magnesium oxide (MgO), both supplied by Casa da Química.
Table II - Rheological parameters of the compositions studied.

| Composition | AV₁ (cP) | PV₁ (cP) | AV₂ (cP) | PV₂ (cP) |
|-------------|----------|----------|----------|----------|
| 1           | 19.75    | 1.00     | 13.50    | 3.00     |
|             | 17.00    | 2.00     | 12.00    | 3.00     |
|             | 17.50    | 7.00     | 27.50    | 6.00     |
| 2           | 20.00    | 6.00     | 26.00    | 7.00     |
|             | 11.00    | 4.00     | 17.00    | 4.00     |
|             | 11.50    | 4.00     | 17.00    | 5.00     |
| 3           | 19.00    | 4.00     | 24.50    | 5.00     |
|             | 18.00    | 4.00     | 22.50    | 4.00     |
|             | 11.00    | 3.00     | 14.00    | 3.00     |
|             | 10.00    | 4.00     | 13.00    | 3.00     |
|             | 17.50    | 6.00     | 31.50    | 9.00     |
| 5           | 18.00    | 5.00     | 29.50    | 8.00     |
|             | 20.00    | 4.00     | 22.00    | 4.00     |
|             | 20.00    | 3.00     | 24.00    | 4.00     |
|             | 17.50    | 3.00     | 20.00    | 5.00     |
| 6           | 20.50    | 5.00     | 22.00    | 4.00     |
|             | 13.00    | 5.00     | 18.00    | 4.00     |
|             | 15.50    | 4.00     | 18.50    | 4.00     |
| 7           | 20.00    | 5.00     | 26.50    | 6.00     |
|             | 20.00    | 6.00     | 24.50    | 5.00     |

Table III - Decoded regression equations for AV₁, PV₁, AV₂, and PV₂.

| Variable | Equation |
|----------|----------|
| AV₁      | AV₁ = 0.19.AM₁ – 0.04.B + 138.91.C – 1.46.AM₁.C + 0.03.AM₁.B.C |
| PV₁      | PV₁ = 0.02.AM₁ + 1.69.B + 1.02.C |
| AV₂      | AV₂ = 0.1.AM₂ + 134160.3.B + 1.6.C – 2039.0.AM₂.B – 675.1.B.C + 7.0.AM₂.B.(AM₂-B) |
| PV₂      | PV₂ = 0.03.AM₂ + 1.33.B + 0.53.C + 1.54.B.C |

Table IV - Statistical parameters of the analyses of variance for the AV and PV variables relative to the selected models.

| Variable | Model          | Test F_cal     | F_cal/F_tab   | p-value | R²   |
|----------|----------------|----------------|---------------|---------|------|
| AV₁      | Special cubic  | 21.0972        | 6.8945        | 0.0000  | 0.8491|
| PV₁      | Linear         | 16.7879        | 4.6762        | 0.0001  | 0.6639|
| AV₂      | Complete cubic | 35.3216        | 11.9330       | 0.0000  | 0.9266|
| PV₂      | 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; R² - correlation coefficient.
III), correlating the mass proportion of clay and MgO and CaCl₂ 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 AV₁, PV₁, and AV₂ showed that the models were not only significant but also predictive. For PV₁, it can be stated that the model was significant [14, 21].

Figs. 1 and 2 illustrate the response surfaces and contour plots for AV₁ and PV₁ 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 Mg²⁺ 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...
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 and PV. The cross-hatched
area indicated the compositions, whose rheological

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

![Figure 4: Response surface (a) and contour plot (b) for AV calculated from the complete cubic model as a function of the amount of clay AM2, MgO, and CaCl2.][Figura 4: Superfície de resposta (a) e curvas de nível (b) para AV, calculadas a partir do modelo cúbico completo em função da quantidade da argila AM2, MgO e CaCl2.]

![Figure 5: Response surface (a) and contour plot (b) for PV calculated from the quadratic model as a function of the amount of clay AM2, MgO, and CaCl2.][Figura 5: Superfície de resposta (a) e curvas de nível (b) para PV, calculadas a partir do modelo quadrático em função da quantidade da argila AM2, MgO e CaCl2.]
parameters $AV_i$ and $PV_i$ 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 $AV_i$ and $PV_i$ were calculated and then determined experimentally [14]. The results are shown in Table V. The predicted and experimentally-measured results for the $AV_i$ and $PV_i$ values were similar, making it possible to state that the statistical models were reliable for predictive purposes. Similar results were obtained in [13].

Figs. 4 and 5 illustrate the response surfaces and contour plots for $AV_i$ and $PV_i$, 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.
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(Rec. 24/05/2019, Rev. 29/07/2019, 13/09/2019, Ac. 16/09/2019)