

DESIGN OF EXPERIMENTS ON SODIC ACTIVATION OF BENTONITE FOR USING AS WATER-BASED DRILLING FLUIDS

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Abstract

The sodic activation of an Algerian bentonite was investigated using a factorial 3^3 experiment design in order to improve the rheological properties in the drilling fluids. Three key parameters were investigated, namely the effects of Na_2CO_3 percentage, the drying time and the temperature. The results showed that in optimal activation conditions (carbonate percentage 3.5%, drying time 65 min and temperature 85°C), the highest viscosity (Reading 600 rpm) was found to be 42 cP. The model adequacy was also verified through additional experiment within the fixed parameters ranges, and was discussed.

The rheological behavior of Na-Bentonite suspensions was investigated in the presence of different polymers; the results indicated that this addition can greatly improve the rheological properties of bentonite dispersions. The addition of 0.4% of CMC in the bentonite dispersions provides an exceptional rheological properties ($R_{600} = 57$ cP, $\text{FV} = 16$ mL and $\text{Ratio} = 4.33$) according to API norms.

Keywords: Bentonite; Rheological properties; Drilling fluids; Factorial design.

1. Introduction

Bentonite minerals have wide range of applications in the different industrial fields such as ceramic, cement, paints, food, drug manufacturing, treating polluted water, such as the adsorption of toxic organic compounds [1-2] and stabilization of oil-water emulsions [3]. Bentonite dispersions are widely used in industrial processes because of their exceptional colloidal and rheological properties. The bentonite is used as an additive to control the water-based drilling fluid properties capable of performing the functions such as: lubricating the drill bit, transporting rock cuttings to surface, applying hydrostatic pressure in the well bore to ensure well safety, and preventing fluid loss into the formations by forming a filter cake on the walls of the well bore [4].

The use of bentonite suspension as a drilling fluid causes a decrease in density and viscosity. But during the operation of drilling fluids, several requirements are imposed: the increase of density, the viscosity, the gelation, and lubricity. The density can be increased by adding the barite and even the viscosity can be also increased by adding some kinds of polymers like xanthan gum, scleroglucan, carboxymethyl cellulose (CMC), polyethyleneimine, polyacrylates and polyacrylamides [4-5]. Also, in order to increase the viscosity and to improve the thixotropic behaviour of bentonite suspensions, Na_2CO_3 , NaOH , $\text{Mg}(\text{OH})_2$ are added to bentonite suspensions [6-8]. Other studies have shown that the addition of electrolytes such as NaCl , Na_2SO_4 , KCl , CaCl_2 , and BaCl_2 in a concentration range of 0.02 to 0.2 M reduced the apparent viscosity of the bentonite suspensions [6].

The effect of soda addition on the rheological properties of bentonites has been widely studied and it was the subject of many previous works [9-13]. Addition of soda increased the viscosity and the thixotropy. Further addition of soda reduced these values again. The effect of Na_2CO_3 on several Argentine bentonites shown an increase of the gel strength and of the

apparent viscosity, this increase was related to the content of the particles and the $\text{Na}^+/\text{Ca}^{+2}$ ratio [11]. The type of flow, the viscosity of clay suspensions are affected by the various factors: the clay concentration, the size and shape of clay particles, the electrostatic properties of clay particles, the exchangeable ions and the type of bentonite [12]. Generally, the flow of bentonite dispersions is very sensitive to the $\text{Na}^+/\text{Ca}^{+2}$ ratio. In practical applications the properties of bentonites can be improved by changing the $\text{Na}^+/\text{Ca}^{+2}$ ratio [13]. The rheological properties of dispersed bentonites depend on the cation that is originally present in the bentonite. A Ca-bentonite dispersed in a sodium salt solution behaves differently from a dispersion of a bentonite in its sodium form in a calcium salt solution, even though the $\text{Na}^+/\text{Ca}^{+2}$ ratio is the same [12].

The first objective of the present study is to determine the influence of Na_2CO_3 on the rheological behavior of the bentonite suspensions. The attempts were made to optimize the sodic activation of an Algerian bentonite using a factorial 3^3 experiment designs in order to improve the clay effectiveness, expressed in terms of viscosity (Reading 600 rpm) in the bentonite suspension. For this purpose, the effects of three key parameters were investigated, namely the effects of the Na_2CO_3 percentage, drying time and temperature. Consequently, the clay viscosity (R_{600}) will be considered as the response-function, and will be prone to modelling, simulation and optimization [14]. One expects that the resulting models will fully describe not only the individual effect of each parameter but also the interactions occurring between two or more factors. The second objective of the present study is to investigate the influence of some polymer, namely the carboxymethylcellulose (CMC), anionic polyacrylamide (Floerger), polysacchadire (Starch) and carbohydrates (Dextrins) on the rheological properties of bentonite dispersions.

2. Experimental

2.1. Bentonite sample

The natural bentonite used in this study was obtained from deposits in the area of Maghnia (west of Algeria). The chemical composition determined by X-ray fluorescence spectroscopy (Philips PW 3710) and was found to be as follows: 62.48% SiO_2 , 17.53% Al_2O_3 , 1.23% Fe_2O_3 , 3.59% MgO , 0.82% K_2O , 0.87% CaO , 0.22% TiO_2 , 0.39% Na_2O , 0.04% As , 13.0% loss on ignition at 950°C . The mineralogical analysis showed that the native crude clay mineral contains preponderantly Montmorillonite (86 wt.%). The clay composition also includes Quartz (10%), Cristoballite (3.0%) and Beidellite (less than 1%) [14-15].

2.2. Reagents

The commercial sodium salts (NaCl , Na_2SiO_2 and Na_2CO_3) were purchased from Aldrich and Sigma and were used as received. The polymers used in this work are as follows:

- CarboxyMethyl Cellulose or cellulose gum (CMC) was supplied by BASP (BAROID Algeria Service aux Puits) Company (Hassi-Messaoud-Algeria). The chemical formula is as follows: $[\text{C}_6\text{H}_7\text{O}_2(\text{OH})_x(\text{OCH}_2\text{COONa})_y]_n$.
- Anionic Polyacrylamide ($\text{C}_3\text{H}_5\text{NO}$)_x, abbreviated as (Floerger) is a polymer formed from acrylamide subunits ($-\text{CH}_2-\text{CH}(-\text{CONH}_2)-$). It was provided from SNF S.A Company (Saint-Etienne-F).
- Starch ($\text{C}_6\text{H}_{10}\text{O}_5$)_n is a carbohydrate consisting of a large number of glucose units joined by glycosidic bonds. This polysacchadire is produced by most green plants as an energy store; it was supplied by ENOF Ltd. Company (Algeria).
- Dextrins ($\text{C}_6\text{H}_{10}\text{O}_5$)_n are a group of low-molecular-weight carbohydrates produced by the hydrolysis of starch. Dextrins are mixtures of polymers of D-glucose units; it was supplied by ENOF Ltd. Company (Algeria).

2.3. Sodic activation of bentonite

Appropriate percentage of sodium salt was added to 100 g of crushed natural bentonite and mixed with a small amount of distilled water until obtaining a paste. The bentonite paste was divided and a small ball was formed. The formed grains of bentonite are put in laboratory

oven for 45 min at fixed temperature (T). After drying, ground bentonite in a ball mill and sieved through a 150 µm sieve prior to use.

2.4. Suspension properties of bentonite-water systems

OCMA grade bentonite is a montmorillonite-based clay which by nature of its source cannot meet all aspects of API Specification 13A-Section 4. This bentonite may have been treated with soda ash, polymer, or other chemicals to improve suspension property performance. OCMA grade bentonite shall be deemed to meet this specification if a composite sample representing no more than one day's production conforms to the physical requirements of

Table.1. OCMA Grade bentonite, Physical requirements

| Requirements | Specification |
|--------------------------------------|--------------------------|
| Suspension Properties | |
| Viscometer Dial Reading at 600 rpm | 30 cP, minimum |
| Yield Point/Plastic Viscosity, Ratio | 6, maximum |
| Filtrate Volume | 16 mL, maximum |
| Residue greater than 75 µm | 2.5 wt. percent, maximum |
| Moisture | 13 wt. percent, maximum |

2.4.1. Equipment

Mixer (Hamilton Beach mixer): Each spindle will be fitted with a single sine-wave impeller approximately one inch (25 mm) in diameter mounted flash side up. Container: Hamilton Beach mixer cup M110-D. The Sealed container: 500 mL with lid. Motor Driven Direct indicating Viscometer as referenced in API RP 13B-1. Filter press: as referenced in API RP 13B-1 (1st edition, June 1990, Par. 3.2). Graduated cylinder (TD): 500±5 mL and 10±0.1 mL.

2.4.2. Procedure

- 600 rpm Dial Reading, Plastic Viscosity, Yield Point

Prepare a suspension of OCMA grade bentonite: add 22.5 g of bentonite to 350 mL of deionized water while stirring on the mixer for 20 min. Age the bentonite suspension up to 16 hours in a sealed or covered container at room temperature. Record storage temperature and storage duration. After aging bentonite suspension, shake well and then pour the suspension into the mixer container. Stir the suspension on the mixer for 5 min. Pour the suspension into the viscometer cup provided with the direct indicating viscometer. The dial readings at 600 and 300 rpm rotor speed settings of the viscometer shall be recorded when a constant value for each rpm is reached.

$$\text{Plastic Viscosity (cP)} = [600 \text{ rpm reading}] - [300 \text{ rpm reading}]$$

$$\text{Yield Point (lb/100 ft}^2\text{)} = [300 \text{ rpm reading}] - \text{Plastic Viscosity}$$

$$\text{Yield Point/Plastic Viscosity, Ratio} = \text{Yield Point} \div \text{Plastic Viscosity}$$

- Filtrate Volume

Recombine all of suspension as prepared and tested and stir in container for 1 min on the mixer, adjust suspension temperature to 25±1°C. Pour the suspension into the filter press cell. Before adding the suspension, be sure each part of the filter cell is dry and that all gaskets are not distorted or worn. Pour the suspension to within about 13 mm of the top of the cell. Complete assembly of the filter press cell. Place filter cell in frame and close relief valve. Place container under the drain tube.

Set one timer for 7.5 min and the second timer for 30 min. Start both timers and adjust pressure on cell at 100 psi (690 kPa). Both of these steps shall be completed in less than 15 seconds. Pressure shall be supplied by compressed nitrogen. At 7.5 min on the first timer, remove the container and any adhering liquid on the drain tube and discard. Place a dry 10 mL graduated cylinder under the drain tube and continue collecting filtrate to the end of the second timer set at 30 min. Remove the graduated cylinder and record the volume of filtrate collected.

Calculate the filtrate volume of the suspension as: $FV (mL) = 2 \times Ve$, where (Ve) is the volume filtrate collected between 7.5 and 30 min.

3. Results and discussion

3.1. Preliminary experiments for sodic activation of bentonite

Before process to sodic activation of bentonite, we evaluated the rheological properties of natural bentonite. The bentonites preparations are realized under the following conditions: $T=80^{\circ}C$ and Time drying = 100 min. Results: 600 rpm Reading (R_{600}) = 12 cP, 300 rpm Reading (R_{300}) = 9 cP, Moisture (H%) = 10.5, $FV = 10.7$ and Ratio = 2.

The results showed that in the natural state, bentonite is not in accordance with API norms. For example, R_{600} present a very low viscosity for ensure a good rheological behavior of suspensions. The sodic activation of bentonite is more than necessary to improve the rheological properties of bentonite suspensions.

In order to choose the best salt which permits a good activation of bentonite, we used three different sodium salts: (A) sodium chloride ($NaCl$), (B) sodium silicate (Na_2SiO_2) and (C) sodium carbonate (Na_2CO_3). The choices of salt which can potentially activate the bentonite allow us to prepare a good quality of drilling bentonite and exhibits properties in accordance with API norms. The bentonites preparations are realized at ($T=80^{\circ}C$ and Time drying = 100 min). The rheological properties of treated bentonites are shown in Table 2.

Table.2. Rheological properties of Na-bentonites

| | 2 % | | | 4 % | | | 5 % | | | 6 % | | | 7 % | | |
|----------------|------|-----|------|------|------|------|------|------|------|------|------|------|------|------|------|
| | A | B | C | A | B | C | A | B | C | A | B | C | A | B | C |
| R_{600} (cP) | 12 | 14 | 20 | 12 | 15 | 30 | 12 | 16 | 24 | 12 | 16 | 21 | 12 | 16 | 21 |
| R_{300} (cP) | 8 | 10 | 15 | 8 | 11 | 25 | 8 | 12 | 19 | 8 | 12 | 17 | 8 | 13 | 17 |
| H (%) | 11.3 | 11 | 11.1 | 11.2 | 11.3 | 11.3 | 11.3 | 11.2 | 10.9 | 11.3 | 11.1 | 11.2 | 11.3 | 11.2 | 11.2 |
| FV (mL) | 13 | 14 | 15 | 13 | 13 | 19 | 13 | 15 | 17 | 13 | 15 | 15 | 13 | 14 | 15 |
| Ratio | 1.0 | 1.5 | 2 | 4.0 | 1.7 | 4.0 | 4.0 | 2.0 | 2.8 | 4.5 | 2.0 | 3.25 | 4.5 | 3.3 | 3.25 |

API norms ($R_{600} \geq 30$, $FV \leq 16$, $Ratio \leq 6$ and $H\% \leq 13$)

From Table 2, the sodic activation of bentonite with $NaCl$ has no effect on the rheological properties of bentonite suspensions. The viscosity R_{600} remains constant and equal to 12 cP (value far from the API norms). The sodic activation of bentonite with sodium silicate (Na_2SiO_2) as salt does not improve the rheological properties of bentonite suspensions. The values obtained of rheological properties are not in accordance with API norms; for example at 7% of salt, the viscosity R_{600} does not exceed 17 cP. In the case of using sodium carbonate (Na_2CO_3) to activate the bentonite, we found that using 4% of carbonate, the viscosity R_{600} is equal to 30 cP (Table 2). The activation of bentonite with 4% of carbonate improves the rheological properties of suspensions. All properties are in accordance with API norms; except for the FV which exceeds 16 mL.

3.2. Experiment Design for sodic activation of bentonite

In our investigations, a series of 27 attempts were made according to a 3^3 experiment factorial design, by varying the percentage of sodium carbonate (X_1), the temperature (X_2) and the drying time (X_3) in suitable parameter ranges. Three variation levels for each parameter were considered as summarized in Table 3.

Table.3. Factor levels used in the 3^3 factorial experiment design

| Factors | Symbol of coded variables | Low level (-1) | Medium level (0) | High level (+1) |
|-----------------------------|---------------------------|----------------|------------------|-----------------|
| Na_2CO_3 (%) | X_1 | 3.5 | 4.5 | 5.5 |
| Temperature ($^{\circ}C$) | X_2 | 60 | 85 | 110 |
| Drying time (min) | X_3 | 60 | 90 | 120 |

3.2.1. Design for bentonite activation

The results of the sodic activation process were expressed in terms of the viscosity Dial Reading at 600 rpm (R_{600}), regarding as being the response function in the investigated process. These results are summarized in table 4.

Table 4. Experimental design and viscosity (R_{600}) of activated bentonite

| Experiment n°. | Factors levels | | | Response function |
|---------------------------|----------------|-------|-------|-------------------------------------|
| | X_1 | X_2 | X_3 | Viscosity 600 rpm Dial Reading (cP) |
| 1 | | | -1 | 36 |
| 2 | | -1 | 0 | 31 |
| 3 | | | 1 | 29 |
| 4 | -1 | | -1 | 38 |
| 5 | | 0 | 0 | 35 |
| 6 | | | 1 | 30 |
| 7 | | | -1 | 35 |
| 8 | | +1 | 0 | 29 |
| 9 | | | 1 | 20 |
| 10 | | -1 | -1 | 32.5 |
| 11 | | | 0 | 30 |
| 12 | | | 1 | 26 |
| 13 | 0 | | -1 | 36 |
| 14 | | 0 | 0 | 34 |
| 15 | | | 1 | 29 |
| 16 | | | -1 | 24 |
| 17 | | +1 | 0 | 22 |
| 18 | | | 1 | 20 |
| 19 | | -1 | -1 | 24 |
| 20 | | | 0 | 22 |
| 21 | | | 1 | 20 |
| 22 | +1 | | -1 | 26 |
| 23 | | 0 | 0 | 22 |
| 24 | | | 1 | 20 |
| 25 | | | -1 | 26 |
| 26 | | +1 | 0 | 23 |
| 27 | | | 1 | 20 |
| (28, 29, 30) ^a | 0 | 0 | 0 | 32.8, 33.6, 34.3 |

^(a) Three additional tests at the central point (0, 0, 0) for the calculation of the Student's t test.

Preliminary observations show that viscosity (R_{600}) varies significantly according to the experiment parameters, reaching values of 36–38 cP under certain operating conditions. From table 4, it already appears that the highest viscosity value (38 cP) was obtained with the use of low carbonate percentage and medium temperature.

3.2.2. Model calculations and refinement

The viscosity (R_{600}) modeling was achieved on the basis of the 27 measured values, using a Taylor's second-order polynomial [14,16]. The model calculations were achieved using non dimensional or reduced values of these variables, each of them being varied on three levels (table 5 summarizes the coefficients values of the model).

Table.5. Model coefficients and their corresponding effects upon viscosity (R_{600})

| Variable | Model | | Expected effect on the Viscosity |
|---------------|-------------|-------|--|
| | Coefficient | Value | |
| $X_0 = 1$ | b_0 | 34 | High average Viscosity of the activated bentonite |
| X_1 | b_1 | -4.39 | (- - -) very weak detrimental individual effect of X_1 |
| X_2 | b_2 | -1.80 | (-) Weak detrimental individual effect of X_2 |
| X_3 | b_3 | -3.47 | (- - -) very weak detrimental individual effect of X_3 |
| $X_1 X_2$ | b_{12} | 1.33 | (+) Very weak favourable interaction of X_1 and X_2 |
| $X_1 X_3$ | b_{13} | 1.08 | (+) Very weak favourable interaction of X_1 and X_3 |
| $X_2 X_3$ | b_{23} | -0.54 | (-) Very Weak detrimental interaction of X_2 and X_3 |
| X_1^2 | b_{11} | -1.22 | Pronounced maximum with respect to X_2 |
| X_2^2 | b_{22} | -3.97 | Very pronounced maximum with respect to X_1 |
| X_3^2 | b_{33} | -0.30 | Slight and flat maximum with respect to X_3 |
| $X_1 X_2 X_3$ | b_{123} | 0.62 | Weak ternary detrimental interaction |

(+) Favourable or positive effect; (-) detrimental or negative effect

The following mathematical model shows the coefficients values (b_i) of the model, supposed to describe the individual effects of parameters, along with their possible interactions.

$$Y = 34 - 4.39X_1 - 1.8X_2 - 3.47X_3 + 1.33X_1X_2 + 1.08X_1X_3 - 0.54X_2X_3 - 1.22X_1^2 - 3.97X_2^2 - 0.3X_3^2 + 0.62X_1X_2X_3$$

The individual effects and interactions of the parameters were discussed on the basis of the sign and the absolute value of each coefficient. These coefficients features will define the strength of the corresponding effect involved and the way it acts upon Viscosity (favourable or detrimental), respectively.

These predictions are in agreement with the shape of the response surface, plotted three times by fixing successively the three parameters at the central values, according to the following equations (Table 6).

Table.6. Specific regression functions with one fixed variable

| Coded variable fixed, $X_i = 0$ | Polynomial model |
|---------------------------------|--|
| $X_1 = 0$ | $Y = 34 - 1.8X_2 - 3.47X_3 - 0.54X_2X_3 - 3.97X_2^2 - 0.3X_3^2$ |
| $X_2 = 0$ | $Y = 34 - 4.39X_1 - 3.47X_3 + 1.08X_1X_3 - 1.22X_1^2 - 0.3X_3^2$ |
| $X_3 = 0$ | $Y = 34 - 4.39X_1 - 1.8X_2 + 1.33X_1X_2 - 1.22X_1^2 - 3.97X_2^2$ |

The vicinity around these central values is supposed to include the optimum, and the resulting 3-D representations of the response function, as illustrated by Fig. 1.

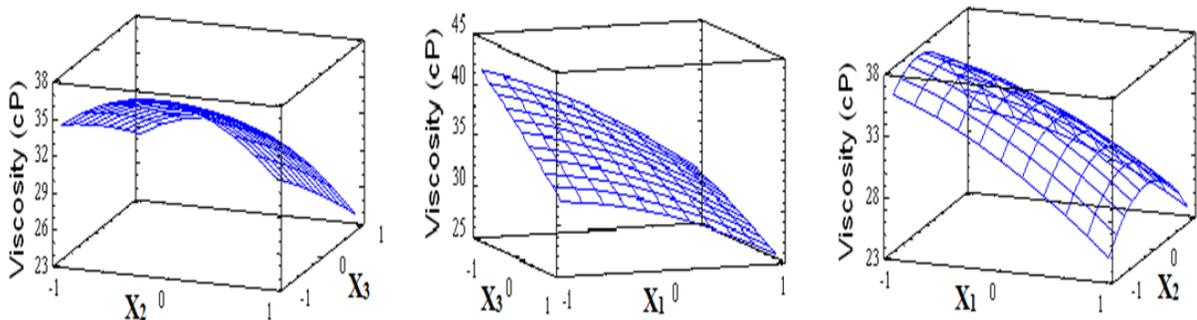


Fig.1. 3D representation of viscosity (R_{600}) of bentonite at fixed ($X_1 = 0, X_2 = 0$ and $X_3 = 0$) X_1 : carbonate percentage; X_2 : Temperature; X_3 : Drying time

For the sake of reproducibility, one must check whether this model accurately describes the process investigated by determining which coefficients could be neglected, through Student's t test and Fisher's test [17-18]. The model adequacy strongly depends on the

accuracy of the experiment. In the current experiment, the main errors arise from volume and weight measurements. For this purpose, three additional attempts at the central point (0,0,0) are required for estimating the average error in the value of each coefficient, on the basis of the random variance. The calculations made are summarized in table 7.

Table.7. Model adequacy tests and variance analysis

| Feature | Symbol | Value |
|--|-----------------|-------------------|
| Average yield at (0,0,0) point | y_0 | 33.57 |
| Random variance | S^2 | 0.56 |
| Square root of variance | S | 0.75 |
| Risk factor (chosen arbitrary) | α | 0.05 (95%) * |
| Student's t test factor | t_v | 4.3 ** |
| Average error on the coefficient value | Δb_i | ± 0.62 at 95% |
| Number of remaining coefficients | R | 8 *** |
| Model response at (0,0,0) | $b_0 (Y_{000})$ | 34 |
| Discrepancy on average yield | d | 0.43 |
| Error on average yield discrepancy | Δd | ± 1.96 |
| Average yield for the 27 attempts | Y_m | 27.35 |
| Residual variance | S_r^2 | 32.89 |

Thus, with a 95% confidence (i.e., $\alpha = 0.05$), and for a 2 variance (i.e., for three attempts at central point), one assessed the value of $t_{v,1-\alpha/2}$ as being equal to (4.3). Therefore, at this (1- α) level, the confidence range for all the coefficients estimated using 27 runs, will be $\Delta b_i = \pm 0.62$ at 95% confidence. From the Student's t tests, it results that $|b_i| < |\Delta b_i|$ for b_{23} , b_{33} and b_{123} . Consequently these coefficients must be removed from the mathematical model because they do not display significant effect upon the response function, being shaded by their average error. Consequently, the resulting new model will be the following:

$$Y = 34 - 4.39X_1 - 1.8X_2 - 3.47X_3 + 1.33X_1X_2 + 1.08X_1X_3 - 1.22X_1^2 - 3.97X_2^2$$

Furthermore, adequacy tests were applied to check whether the model calculated is valid within the parameter ranges investigated. For this purpose, a first method of adequacy calculations [18-19] showed that d , the discrepancy between the average viscosity value, $y_0 = 33.57$, and the model response for the additional three attempts at the (0, 0, 0) point is smaller than Δd , indicating that the model can be applied within the whole range investigated.

3.2.3. Parameters optimization

From the above polynomial model, the highest viscosity was obtained with a bentonite whose activation was performed at low values of carbonate percentage and drying time, but at medium temperature. Graphical determination was achieved using 2D representation of viscosity (R_{600}) a function of the carbonate percentage and drying time, maintaining constant the temperature at its medium value, supposed to be in the vicinity of the optimum value (Fig. 2).

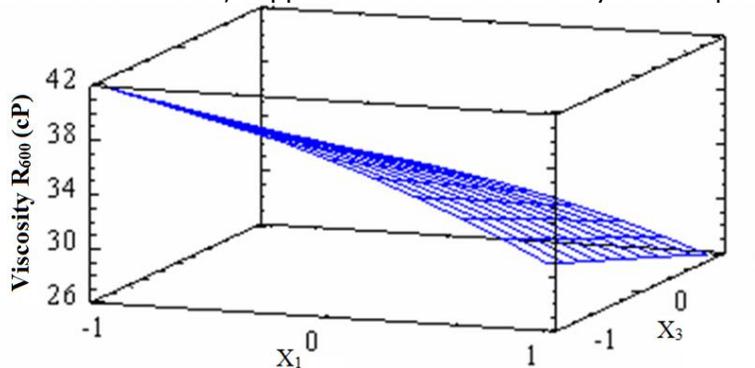


Fig.2. 3D representation of the viscosity (R_{600}) of bentonite at fixed $X_3 = 0$; X_1 : Carbonate percentage; X_2 : Drying time

A more precise method for determining the optimum parameter values should consist of derivation of the polynomial model, and the results obtained are summarized in table 8. The results obtained by both methods are in agreement, confirming once again that neglecting the effect of the third factor, namely the solid to liquid phase ratio does not affect the model accuracy.

Table.8. Optimum activation parameters for highest viscosity (R_{600})

| Parameter | Coded variable | Non dimensional values | Real optimum values |
|----------------------|----------------|------------------------|---------------------|
| Carbonate percentage | X_1 | -1 | 3.5 % |
| Temperature | X_2 | 0 | 85°C |
| Drying time | X_3 | -0.85 | 65 min |

Here, one must emphasize that the optimization calculations gave values included within the respective selected ranges (carbonate percentage = 3.5%, temperature = 85°C and drying time = 65 min), confirming once again the judicious choice of the parameters ranges and the applicability and accuracy of the model developed to describe the correlation between the bentonite activation factors and its performances in bentonite-water systems. Under these conditions, a viscosity (R_{600}) value of 42 cP was obtained.

In our opinion, these results were satisfactory, considering that there is no need for additional factorial design with more severe activation parameters. Few additional attempts, performed around the calculated X_{opt} values, these experimental data agree with those calculated and can be regarded as nearly similar.

3.3. Effects of the parameters

3.3.1. Effect of the carbonate percentage

In a second step of the present study, one has performed additional attempts in order to verify the model validity, reproducibility and accuracy. Thus, the viscosity (R_{600}) of various bentonite samples activated at different carbonate percentage but at fixed temperature and drying time in the vicinity of the calculated optimum. The results are plotted in Fig. 3-a.

Thus, it clearly appears that, as expected, the increase of carbonate percentage improves the viscosity (R_{600}) up to nearly 42 cP, for carbonate percentage of ca. 3.5%. Beyond this value an important reduction in viscosity (R_{600}) was observed. The sodium carbonate addition produces a cations exchange between Ca^{2+} of bentonite and Na^+ of carbonate, the Ca^{2+} has an affinity of adsorbed the water and consequently viscosity increases. After the saturation solution by Ca^{2+} , the Na^+ cations in excess react with the OH^- and causes the release of a quantity of H_2O and consequently viscosity decreases.

3.3.2. Effect of the temperature

Similarly, the effect of the temperature upon the viscosity (R_{600}) was examined at fixed carbonate percentage and drying time. As illustrated by Fig. 3-b, maximum viscosity effectiveness or nearly 42 cP, was obtained at 85°C, in agreement with the calculated data.

The viscosity (R_{600}) increases with the increase of temperature until 85°C, beyond this value viscosity decreases. With increase of temperature, the departure of adhesion water related to the lattice crystal and which ensures the particles mobility has a negative influence on viscosity. Thus there is a threshold of drying temperature of not to exceed.

3.3.3. Effect of the drying time

The dependence of the viscosity (R_{600}) on the drying time is given in Fig. 3-c. The viscosity increases with the increase of drying time until 65 min; beyond this value a reduction was observed. The highest viscosity (R_{600}) was obtained with drying time of 65 min, which justified the choice of this value like optimal. A prolonged drying time reduces viscosity slightly. The study of individual effects of various parameters by additional experiments confirms the results found by optimization; Then the optimum conditions for sodic activation of bentonite are:

carbonate percentage = 3.5%, Temperature = 85°C and drying time = 65 min; the viscosity (R_{600}) under these conditions reaches a value of 42 cP.

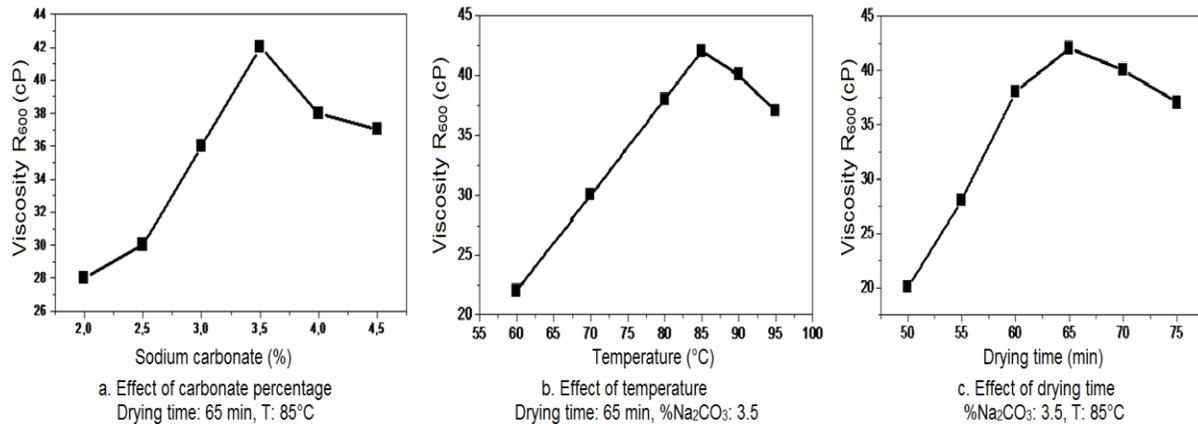


Fig.3. Influence of the parameters on the viscosity (R_{600}) of bentonite suspensions

The activated bentonite sample that displayed the highest effectiveness was fully characterized, and the results of rheological properties were found to be as follows: (R_{600} = 42 cP, R_{300} = 26 cp, Moisture = 10.3%, FV = 22 mL and Ratio = 3.33).

All parameters of bentonite dispersions are in agreement with API norms, except for the FV (>16 mL). Therefore it's necessary to add some additives to bentonite in order to reduce the volume filtrate. These additives may be the polymers such as CMC.

3.4. Influence of polymers addition on the rheological properties of bentonite dispersions

The rheological behavior of Na-Bt suspensions was investigated in the presence of different polymers (CMC, Floerger, Starch and Dextrin). There may be two reasons for the increase in rheological properties. First one is the interaction between bentonite particles and polymer and the second one is the increase in the polymer percentage. The extent of interaction of bentonite particle polymer can be influenced by a number of parameters, such as polymer concentration, molecular weight, and functional groups of polymer, degree of hydrolysis of polymer, bentonite-water ratio, and surface charge of bentonite particles, pH and temperature-among others [20-24].

Adsorption of polymer onto bentonite can happen, if it has preferential affinity to the surface in comparison to the affinity of molecules water. In fact, adsorption is a competition between these two agents present in the system to reach the adsorbent. The polymer adsorption alters the structure of the dispersion in the vicinity of the surface [20-21].

Forces responsible for adsorption of polymers result mainly from three types of bonding, namely, electrostatic, hydrogen and covalent bonding [22]. The predominance of any of the above mechanisms over the others depends on the particular bentonite polymers system and the properties of the aqueous medium. Under favorable conditions, various type of mechanism could be operative.

In general polymer adsorption has been reported to be irreversible. However, some solvents can affect irreversibility of the polymer adsorption process. The rate of polymer desorption is also influenced by the porous nature of the clay (large specific surface area). Concentration of the polymer can also affect the reversibility of polymer adsorption.

In polymer adsorption, only the bentonite surface is involved, not the interlayer's. This phenomenon is due to the irregular form of the polymer [23].

Ruehrwein and Word were the first to propose that polymeric flocculants function by a bridging mechanism [24]. Bridging is considered to be a consequence of the adsorption of segments of individual polymeric flocculants molecules onto the surface of more than one

particle. Such bridging links the particles together into loose aggregates which often sediment rapidly. In order to make bridging aggregation of a polymeric flocculants, only adsorption of macromolecules on clay particle surfaces is not enough; in addition, the loops of adsorbed polymer molecules on surfaces must interact with each other's or it is necessary that the loops should extend to surfaces of other particles.

This requires the spatial extension of the loops of the polymeric flocculants to span at least the distance over which the electrostatic repulsion between particles is operative. This distance is of an order equal to the sum of the thicknesses of the electrostatic double layers surrounding the approaching colloidal particles, which is usually appreciable [20].

3.4.1. Influence of CMC addition on the rheological properties of bentonite

The appropriate quantity of CMC was added to bentonite treated with 4% of sodium carbonate. The results of rheological properties were shown in Table 9.

Table.9. Influence of CMC percentage on the rheological properties of bentonite

| CMC (%) | 0 | 0.1 | 0.2 | 0.3 | 0.4 | 0.5 | 0.6 | 0.7 | 0.9 | 1 |
|-----------------------|------|-----|------|------|------|-----|-----|------|------|----|
| R ₆₀₀ (cP) | 32 | 41 | 51 | 53 | 57 | 67 | 70 | 80 | 86 | 95 |
| R ₃₀₀ (cP) | 26 | 35 | 40 | 45 | 48 | 57 | 60 | 69 | 71 | 76 |
| FV (mL) | 22 | 18 | 18 | 17 | 16 | 15 | 15 | 15 | 13 | 13 |
| Ratio | 3.33 | 4.8 | 2.63 | 4.62 | 4.33 | 4.7 | 5 | 5.27 | 3.73 | 3 |

The results indicated that CMC addition can greatly improves the rheological properties of bentonite dispersions. The viscosity increases with percentage of CMC and achieved extraordinary values (R₆₀₀ reaches 90 cP at 1% of CMC). The FV of bentonites dispersions decrease with addition of CMC (at 0.4% of CMC, the FV valued is 16 mL). From 0.4 to 1% of CMC, the values of FV are in accordance with API norms. For the ratio, it always in accordance with API norms whatever the percentage of CMC used. So, it can be considered that the addition of 0.4% of CMC in the bentonite dispersions provides an exceptional rheological properties according to API norms (R₆₀₀ = 57 cP, FV = 16 mL and Ratio = 4.33). CMC solutions are known to be strongly time-dependent materials, which mean that they exhibit a viscosity–time relationship, where the viscosity decreases with the time [25-26].

The time-dependent behavior of the viscosity is related to changes occurring in the inner structure of the fluid due to particle interaction forces like the Van de Waals forces, which are responsible for the formation of flock and aggregates. These forces act at microscopic scale between dispersed species in the material and, above a certain particle volume fraction, may lead to the formation of a rigid continuous particle network, which can withstand the flow [4]. The increase in viscosity was due to interactions between CMC molecules with water, we think that the observed increase in viscosity could be interpreted as the result of a stiffer inner structure due to the formation of entanglements of CMC coils and the increase in the intermolecular interactions.

Also, interactions between CMC molecules with bentonite particles increase viscosity (the appearance of micelles acting as cross links between the particles of bentonite). The addition of CMC influences on the FV essentially by three different mechanisms:

A deflocculated cake settles to form a thinner and impermeable cake so that the molecules of CMC act as deflocculates; If the liquid phase, which is passed through the cake, is viscous, it will also reduce the filtrate; Also, the added CMC particles can be transformed and compressed to seal the pores of the cake.

3.4.2. Influence of Floerger addition on the rheological properties of bentonite

The appropriate quantity of Floerger was added to bentonite treated with 4% of sodium carbonate. The results of rheological properties were shown in Table 10.

Table.10. Influence of Floerger percentage on the rheological properties of bentonite

| Floerger (%) | 0 | 0.1 | 0.2 | 0.3 | 0.4 | 0.5 |
|-----------------------|------|-----|------|------|------|------|
| R ₆₀₀ (cP) | 32 | 80 | 111 | 115 | 119 | 121 |
| R ₃₀₀ (cP) | 26 | 70 | 90 | 100 | 105 | 106 |
| FV (mL) | 2 | 16 | 16 | 14 | 14 | 13 |
| Ratio | 3.33 | 6 | 3.28 | 5.66 | 6.05 | 6.06 |

The rheological behaviour can be influenced by Floerger addition in bentonite dispersions. The viscosity increases with percentage of Floerger and achieved very high values (R₆₀₀ reaches 121 cP at 0.5% of Floerger).

There may be two reasons for the increase in viscosity values. First one is the interaction between bentonite particles and Floerger and the second one is the increase in the Floerger percentage. There were some electrostatic interactions between the bentonite layers for the all percentage range of Floerger. But, the number of Floerger molecules adsorbed on the surface of bentonite particles or placed in between the bentonite layers increased as the percentage of Floerger molecules increased in the suspension. Floerger molecules are not able to interact electro-statically with the negatively charged Na-Bt particles because it is a non-ionic water soluble polymer which consists of polar Floerger units [6,27]. These molecules can be adsorbed on the surface of Na-Bt by H-bond formation or they can place between the layers of bentonite.

This results in a screening effect on the surrounding of charged bentonite surfaces which may reduce the electrostatic interactions between the bentonite particles [27].

For the FV, a significant decrease was observed with increasing of Floerger percentage. Only with 0.1% of Floerger, the values of FV are in accordance with the API norms. So, it can be considered that the addition of 0.1% of Floerger in the bentonite dispersions provides an exceptional rheological properties according to API norms (R₆₀₀=80 cP, FV=16 mL and Ratio=6).

3.4.3. Influence of Starch addition on the rheological properties of bentonite

The appropriate quantity of Starch was added to bentonite treated with 4% of sodium carbonate. The results of rheological properties were shown in Table 11.

Table.11. Influence of Starch percentage on the rheological properties of bentonite

| Starch (%) | 0 | 0.1 | 0.2 | 0.3 | 0.4 | 0.5 | 0.6 | 0.7 | 0.9 | 1 |
|-----------------------|------|-----|------|------|------|------|------|-----|------|-----|
| R ₆₀₀ (cP) | 32 | 35 | 35 | 35 | 36 | 35 | 35 | 36 | 35 | 36 |
| R ₃₀₀ (cP) | 22 | 31 | 31 | 32 | 33 | 31 | 32 | 32 | 32 | 32 |
| FV (mL) | 22 | 22 | 22 | 22 | 22 | 22 | 22 | 22 | 22 | 22 |
| Ratio | 3.33 | 6.0 | 6.55 | 9.66 | 10.0 | 6.75 | 9.66 | 7.0 | 9.66 | 7.0 |

The results show that just with 0.1% of Starch, we observe an improvement in the rheological behaviour of the bentonite (R₆₀₀ reaches 35 cP). Above 0.1%, no improvement in rheological properties was observed.

Although the viscosity was increased, the FV is not in accordance with norms and any influence of Starch addition on this property was observed. So we can consider that the best rheological behaviour was obtained with 0.1% of Starch (R₆₀₀=35 cP, FV=22 mL and Ratio=6).

From chemical composition points of view, the Starch resembles a gel structure and it is a linear protein, which is made of various pyrrolidone rings [22-23]. It dissolves in water exhibiting various hydrophilic structures and can be curled like a ball. The Starch adheres on clay surfaces when added into bentonite water system and absorbs water by swelling in slurry and consequently, viscosity of the system increases while fluidity decreases.

The Starch forms like a gel structure together with bounded water molecules to it and absorbed clay minerals. Na-Bt has the ability to form a gel because of its high swelling property. The swelled particles can be disintegrated after some time giving numerous small particles thus, a large surface area. If the Na-Bt water system is prepared as slurry which

provides a large interaction between the particles, viscosity and binding water increase and a physical, reversible gel can be formed as a cluster.

Besides, the repulsive electrostatic and van-der Waals forces, which bring the particles to equilibrium state, contribute to gel formation. The gel strength depends on the thixotropy of slurry [28-29].

3.4.4. Influence of Dextrins addition on the rheological properties of bentonite

The appropriate quantity of Dextrins was added to bentonite treated with 4% of sodium carbonate. The results of rheological properties were shown in Table 12.

Table.12. Influence of Dextrins percentage on the rheological properties of bentonite

| Dextrins (%) | 0 | 0.1 | 0.2 | 0.3 | 0.4 | 0.5 | 0.6 | 0.7 | 0.9 | 1 |
|-----------------------|-----|-----|-----|-----|------|-----|-----|-----|-----|-----|
| R ₆₀₀ (cP) | 39 | 39 | 40 | 40 | 40 | 40 | 39 | 40 | 39 | 39 |
| R ₃₀₀ (cP) | 34 | 34 | 35 | 35 | 35 | 34 | 34 | 35 | 34 | 34 |
| FV (mL) | 21 | 21 | 21 | 21 | 21 | 21 | 21 | 21 | 21 | 21 |
| Ratio | 5.4 | 6 | 6 | 6 | 4.66 | 5.8 | 6 | 6 | 5.8 | 5.8 |

The addition of (0.2–0.5%) of the Dextrins can greatly improves the rheological properties of bentonite dispersions (viscosity R₆₀₀ reaches 40 cP). Above 0.5% of dextrin, no improvement in rheological properties was observed.

The FV value remains constant (equal to 21 mL), this property does not affected by Dextrins addition. For the ratio, it always in accordance with API norms whatever the percentage of Dextrins used. So, it can be considered that the addition of 0.4% of Dextrins in the bentonite dispersions provides the best rheological behaviour (R₆₀₀=40 cP, FV= 21 mL and Ratio= 4.66).

4. Conclusion

Optimized sodic activation of the Algerian bentonite gave rise to an effective drilling bentonite in water-based drilling fluids suspensions. The highest rheological properties and a model for sodic activation of bentonite were investigated by means of 3³ factorial design in order to prepare a drilling bentonite according API norms. The result provides clear evidence that the Na₂CO₃ percentage and drying temperature influence greatly the viscosity of bentonite. The investigated parameters also revealed binary interactions that must not be neglected. The highest viscosity (R₆₀₀) of bentonite suspension was found to be ca. 42 cP, under optimum activation conditions, namely: carbonate percentage (3.5%), temperature (85°C) and drying time (65 min). The polynomial model developed herein for the rheological properties of bentonite may provide a valuable basis for industrial scale applications.

The rheological behavior of Na-bentonite suspensions was investigated in the presence of different polymers (CMC, Floerger, Starch and Dextrins). The results indicated that polymer addition can greatly improves the rheological properties of bentonite dispersions. The viscosity increases with percentage of polymers and achieved extraordinary values. The addition of 0.4% of CMC in the bentonite dispersions provides an exceptional rheological properties according to API norms (R₆₀₀=57 cP, FV=16 mL and Ratio=4.33).

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