

Characterization and Rheological Study of a Tunisian Bentonite for its Use in the Drilling Fluids

OUSSEYNOU M'BODJ, MOUNIR AYADI, MEMIA BENNA†
NAJIA KBIR ARIGUIB* and MALIKA TRABELSI AYADI†

*LPC, Institut National de Recherche Scientifique et Technique
BP 95, 2050 Hamman-lif, Tunisia
E-mail: ariguib@planet.tn*

The Jebel Shemsi ore contains 81% of clays; mainly quartz and carbonate are present as impurities. The dominant phase in the clay fraction is smectite (80%), it also contains illite (15%) and some kaolinite. The cationic exchange capacity (CEC) value of the purified clay is 87 meq/100 g of calcined clay; the total specific surface area (S_T) is equal to 711 m²/g. The dehydration (hygroscopic water) of the raw and purified clay occurs around 109°C and its dehydroxylation at 502°C for the raw bentonite and at 468°C after purification. The study of the clay percentage (w/w) effect on the rheological properties shows that the flow curves have a Newtonian behaviour for the clay percentage lower than 10%. After this percentage, the behaviour becomes rheofluidifiant. The effect of pH on the rheological properties has been studied at the clay percentage of 10% and shows two states of maximum interaction in acidic medium (pH range 2–4) and basic medium (pH range 9.5–11). The suspensions corresponding to the first maximum are gels and exhibit a rheofluidifiant behaviour, whereas those corresponding to the second basic maximum are gels but flow easily and exhibit a Newtonian behaviour. The natural pH of the clay (pH = 7.2) corresponds to the minimum of interactions.

Key Words: Clay, Illite-smectite, Bentonite, pH, Rheology, Stress, Viscosity, Shemsi.

INTRODUCTION

Tunisia has several deposits of bentonites. It is known that this kind of swelling clays are widely used in drilling fluids as the system clay and water can form a good component of these fluids when the clay has some specific properties. To define the possibility of the use, in drilling fluids, of the Tunisian clay provided from Jebel Shemsi in the west-southern Tunisia, it is necessary to proceed, at first, to the physico-chemical characterization of raw bentonite and of the pure clay fraction contained in this bentonite, then to determine the rheological characteristics of these materials.

To relate this study to the industrial conditions, this investigation is carried out using a second bentonite provided by an industrial drilling fluid maker; it is from Wyoming in the USA. This bentonite is considered as a reference. The basic techniques must permit the identification of the Jebel Shemsi and the Wyoming bentonites. The rheological measurements may lead to determine the availability of the Tunisian clay as a component of drilling fluids.

†Faculté des Sciences de Bizerte, 7021 Zarzouna, Tunisia.

This study contains two parts; the first one concerns the complement of the Jebel Shemsi clay characterization and the second one includes the investigation on the rheological properties of this clay as a function of its percentage and of the pH in the clay aqueous suspensions.

EXPERIMENTAL

The characterization was carried out on the raw bentonites ground and sieved at 100 μm and on the purified sodium exchanged clays¹ sieved at 63 μm .

The raw clays will be noted Shb for the clay of Jebel Shemsi and Wb for the clay of Wyoming respectively Shp and Wp.

The methods and techniques used are chemical analysis, X-ray diffraction, infrared spectroscopy, thermal analysis (DTA and TGA), and measurement of cation exchange capacity (CEC) and total specific surface area. The chemical analysis of calcined (at 1000°C) samples was made in order to evaluate Si, Al, Fe, Mg, Ca, Na, Mn, Ti, P and K oxides content. It was carried out by using atomic absorption spectrophotometer, Perkin-Elmer 560. The X-ray diffraction patterns were obtained using a Philips PW 1710 with Cu-K α radiation. The X-ray diffraction was performed on powder or on oriented samples prepared by depositing a clay suspension onto a glass slide. The oriented samples were air-dried, glycolated and heated at 550°C.

The infra-red spectra were obtained by a spectrophotometer FTIR Perkin-Elmer 1000 in the range 4000–350 cm^{-1} . The DTA-TGA were run in a SETARAM TG/DTA 92 apparatus using a sample weight of about 15 mg, at a heating rate of 10°C/min in argon, with alumina as reference. The pH is measured by a Hanna instrument pH-meter.

The cation exchange capacities (CEC) were determined using a method which consists of saturating the clay with cupric ethylene diamine². The total specific surface area of the samples has been measured by the isotherm of methylene blue³.

The preparation of all aqueous suspensions concerning the effect of clay fraction on the rheological properties has been made by mixing the clay with water, shaking the suspensions during 2 h and then left for 24 h.

To study the effect of the pH on the rheological properties, the suspensions have been prepared by avoiding direct contact of the clay powder with acidic (or basic) solution in order to prevent an acidic (or basic) attack on the clay structure. The clay has been mixed with distilled water and shaken for 2 h. After that, the acidic (or basic) solution is added to the obtained suspension and the mixture has been then shaken for another 2 h then left for 24 h. The electrolytes used to vary the pH are HCl and NaOH.

The viscosity and the shear stress were measured on a rheometer provided by Rheologica Instruments, AB Stress Tech.; the geometry used is only the coaxial cylinders.

RESULTS AND DISCUSSION

Chemical analysis: Chemical analysis performed in our laboratory by the reported method⁴ and in the present work, the average structural formula of the Na-exchanged purified sample Shp calculated by Mauguin's method⁵ is as:



They also lead to determine the percentage of smectite in the clay fraction; this percentage equals 80% and that of illite is 15%.

X-ray diffraction: The X-ray diffraction patterns of Shb clay (Fig. 1) contain:

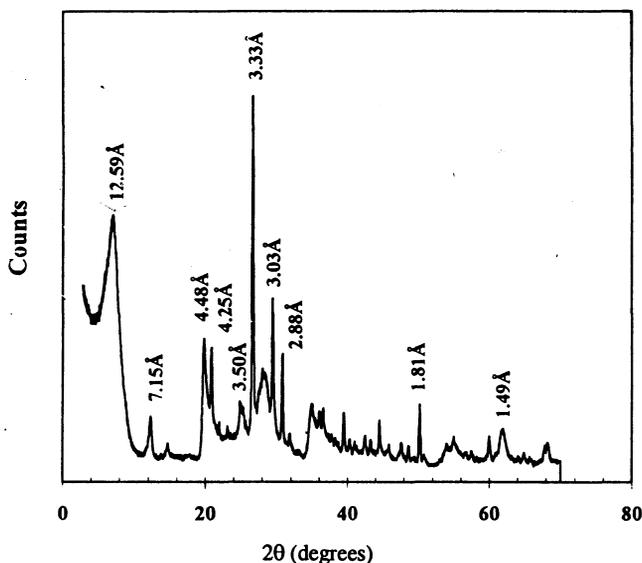


Fig. 1. X-ray diffraction patterns of Jebel Shemsi raw powder clay

- a peak at 12.59 Å corresponding to the 001 reflection of a sodium smectite,
- a peak at 1.49 Å related to the 060 reflection, showing that the smectite is dioctahedral,
- two low intense peaks at 7.15 Å and 3.5 Å attributed respectively to 001 and 002 reflections of kaolinite,
- a peak at 3.35 Å corresponding to the quartz (major impurity),
- a peak at 3.03 Å corresponding to calcite.

Therefore this X-ray pattern indicates the presence of a natural sodium smectite mixed with a small quantity of kaolinite. The impurities are mainly composed of quartz and calcite.

The X-ray diffraction patterns of Wb clay (Fig. 2) show:

- a peak at 14 Å corresponding to the 001 reflection of a calcique smectite,
- a peak at 1.49 Å related to the reflection 060, showing that the clay is dioctahedral,
- a peak at 3.331 Å corresponding to the quartz.

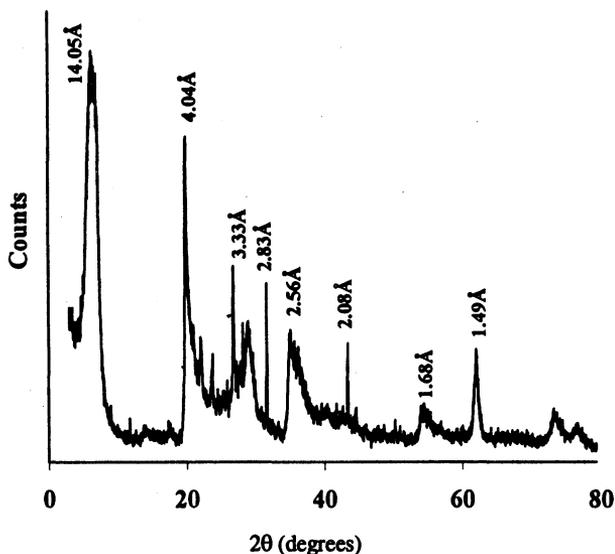


Fig. 2. X-ray diffraction patterns of Wyoming raw powder clay.

Therefore the X-ray diffraction investigation leads us to conclude that the industrial Wyoming clay is calcium dioctahedral smectite and it contains quartz as a major impurity.

The Shp air dried oriented slide diffractogram (Fig. 3a) includes:

- a peak at 12.29 Å corresponding to the 001 reflection; it shows that the clay is a sodium smectite or an interstratified smectite illite⁶;
- two peaks at 7.15 Å and 3.5 Å which can be attributed to kaolinite⁷.

The Shp heated (at 550°C) oriented slide diffractogram (Fig. 3b) reveals that

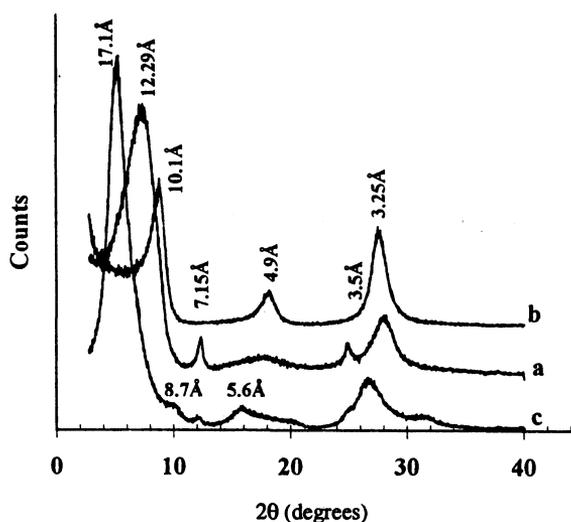


Fig. 3. Diffractogram of the Shp clay oriented on glass slide
(a) air dried oriented slide, (b) heated slide (550°C) (c) ethylene glycol treated slide

the peak at 12.29 Å is shifted at 10.1 Å and the absence of the peaks at 7.15 Å and 3.5 Å, confirming the presence of kaolinite⁶.

The Shp oriented slide treated with ethylene glycol and the X-ray pattern (Fig. 3c) shows:

- a peak at 17.1 Å corresponding to 001 reflection of a swelled smectite, and
- a 002 reflection at 8.7 Å which shows that the Shp clay is an interstratified smectite-illite with a percentage of smectite equal to 84%⁸.

The X-ray diffraction carried out on the Wp clay (Fig. 4a, b and c) shows:

- for the air dried oriented slide (Fig. 4a), three peaks at 12.29 Å; 6.21 Å and 3.2 Å corresponding respectively to 001, 002 and 004 reflections of a sodium smectite.

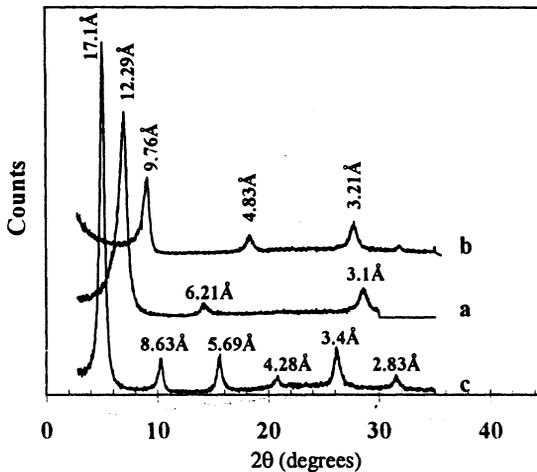


Fig. 4. Diffractogram of the Wp clay oriented on glass slide (a) air dried oriented slide (b) heated slide (550°C)(c)- ethylene glycol treated slide

- for the slide heated at 550°C (Fig. 4b) three peaks at 9.76 Å (001); 4.83 Å (002) and 3.21 Å (003) corresponding to the collapsed interlayers.
- for the slide treated with ethylene glycol the (001), (002), (003), (004), (005) and (006) reflections respectively at 17.1 Å, 8.6 Å, 5.69 Å, 4.28 Å, 3.4 Å and 2.83 Å characterizing a smectite.

The X-ray diffraction results permit to conclude that the Wp clay is a smectite, whereas the Shp clay is probably an interstratified smectite-illite with a little amount of kaolinite.

Cation exchange capacity and specific surface area

The Shp C.E.C. and specific surface area (Table-1) are comprised in the ranges of smectite.

Because of the presence of impurities the C.E.C. of the raw clay Shb (Table-1) is less important than that of the purified one.

According to Gaboriau⁹ the amount of impurities can be estimated from the C.E.C. values of the raw and purified clays. From the preceding results (Table-1) this amount is evaluated to 19%.

Infrared spectroscopy

The IR spectrum (Fig. 5b) of the crude sample Shb confirms the dominant presence of dioctahedral smectite with the Al-Al-OH stretching and bending

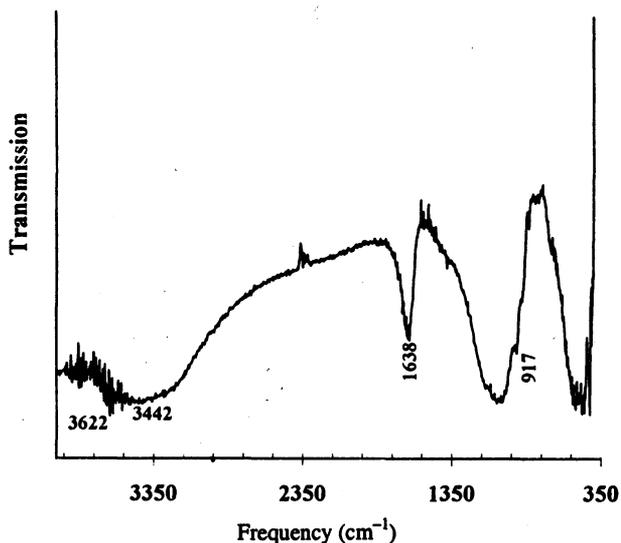


Fig. 5a. Infrared spectra of the Shp clay

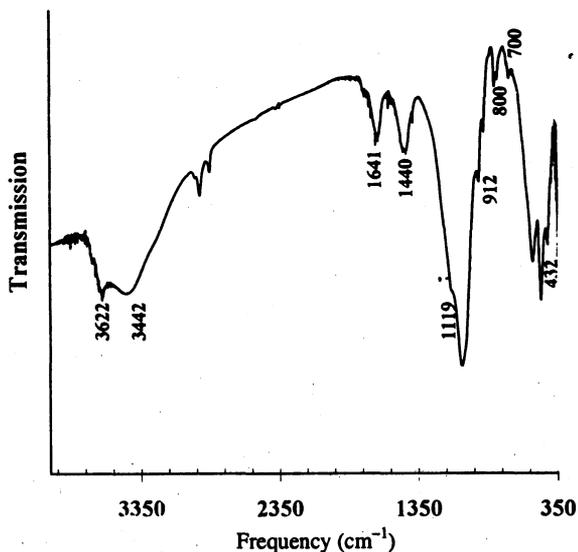


Fig. 5b. Infrared spectra of the Shb clay

bands at 3622 and 912 cm^{-1} respectively^{12,13}. The spectrum shows a band at 3442 and another band at 1641 cm^{-1} corresponding to O—H (hydration water) stretching and O—H bending bands respectively. The doublet at 700 and 432 cm^{-1} is related to the kaolinite⁹, while the doublet at 800 and 780 cm^{-1} is attributed to the quartz. The band at 1440 cm^{-1} reveals the presence of calcite.

TABLE-I
CATION EXCHANGE CAPACITY OF THE JEBEL SHEMSI CLAY

	C.E.C. (meq/100g of calcined clay)	Calculated* C.E.C. (meq/100g of calcined clay)	Impurities (%)‡	Sr (m^2/g)
Shb	70	—	19	—
Shp	87	88.7		711
Smectite	(80–150)‡			(700–800)**

*From chemical analysis results

†Calculated from the measured C.E.E. values

‡Grim 1953 (Ref. 10).

**Calvert 1989 (Ref. 11)

The purified sample Shp (Fig. 5a) gives the same IR spectra as the crude one except that the bands corresponding to the impurities have disappeared after purification.

The IR spectra of the crude Wyoming clay (Fig. 6b) indicates the presence of dioctahedral smectite, with Al—Al—OH stretching and bending bands at 3612 and 910 cm^{-1} respectively. These spectra show the O—H (hydration water) bands at 3440 and 1638 cm^{-1} . The presence of quartz and carbonate is characterized by the bands at 800 and 1452 cm^{-1} respectively; these two bands disappear, as expected, after purification (Fig. 6a).

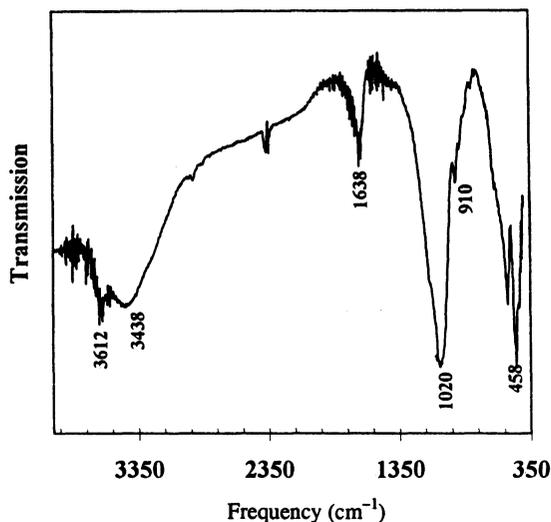


Fig. 6a. Infrared spectra of the Wp clay

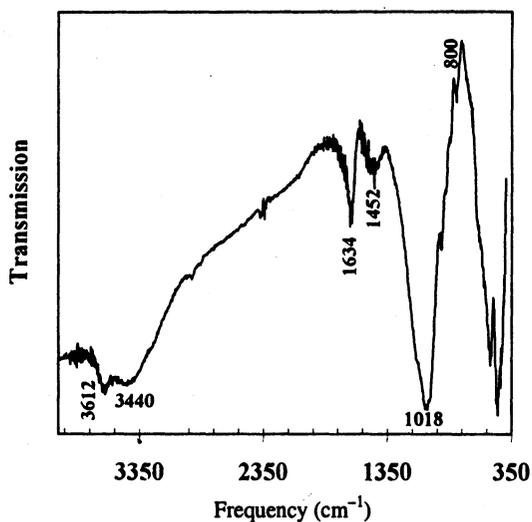


Fig. 6b. Infrared spectra of the Wb clay

Thermo-gravimetric and differential thermal analysis

The DTA and TGA thermograms of the Jebel Shemsi clay (Figs. 7a, 7b) contain:

- Endothermic peaks at 109 and 108°C for Shb and Shp respectively corresponding to the loss of hygroscopic water.
- Peaks at 502 and at 468°C for Shb and Shp respectively corresponding to

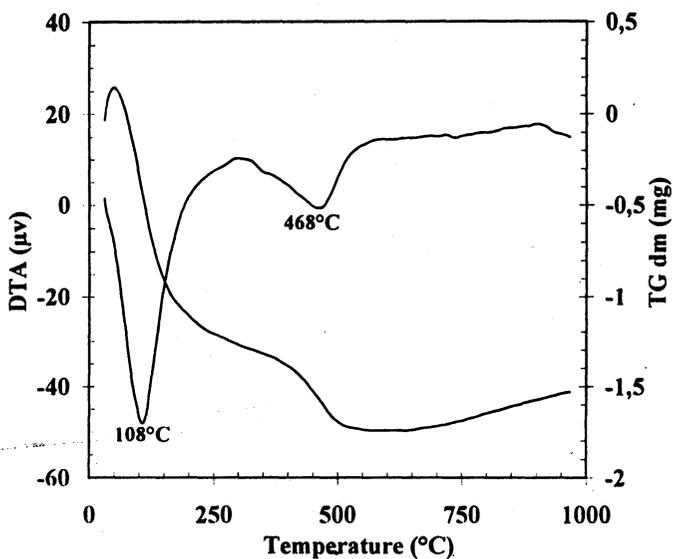


Fig. 7a. DTA/TG curves of the Shp clay

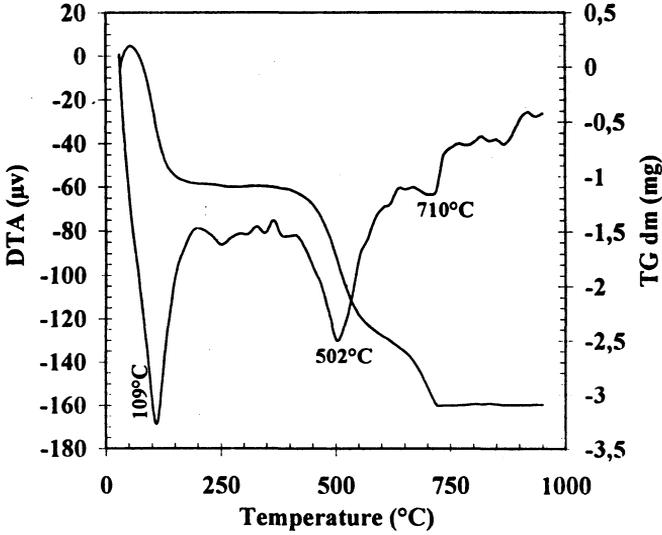


Fig. 7b. DTA/TG curves of the Shb clay

the clay dehydroxylation. These temperatures are lower than what is expected for a pure smectite; this can be explained due to the presence of illite.

A peak at 710°C for Snb due to dissociation of carbonates; it disappears, as expected, after purification.

The TGA/DTA curves of Wp and Wb are shown in Figs. 8a, 8b.

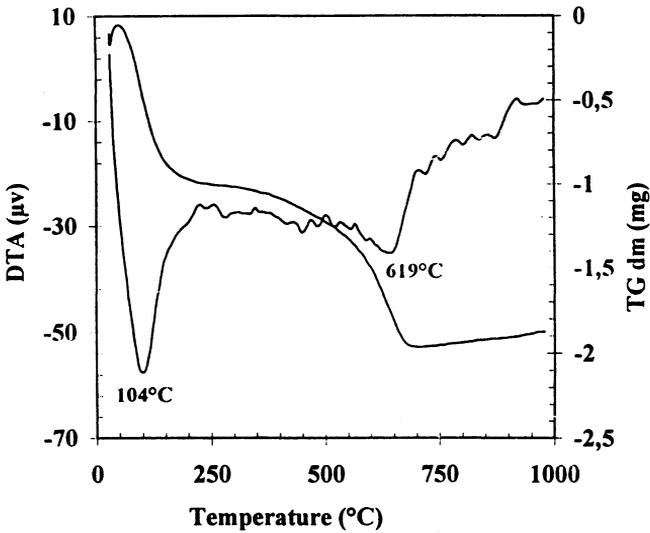


Fig. 8a. DTA/TG curves of the Wp clay

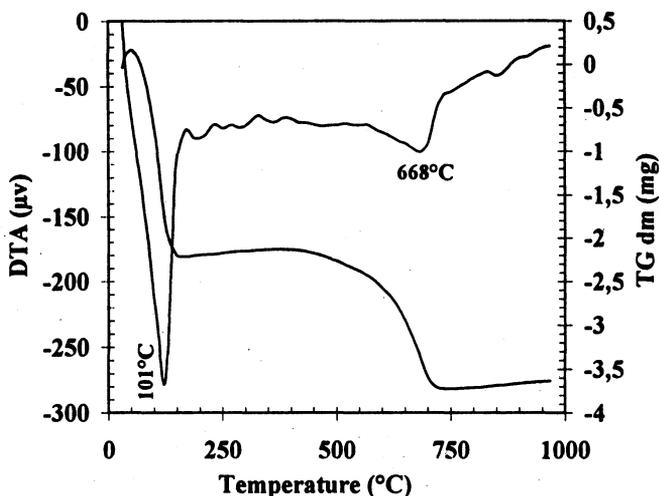


Fig. 8b. DTA/TG curves of the Wb clay

- Endothermic peaks at 101°C for Wb and at 104°C for Wp, corresponding to the loss of hygroscopic water (essentially interlayer).
- Peaks at 668°C for Wb and 619°C for Wp related to the clay dehydroxylation in accordance with the smectite dehydroxylation temperature range (600–700°C)^{12, 14}.

Rheological properties

The rheological measurements were done on the purified clays Shp and Wp. The effect of clay fraction and pH on the rheological properties has been studied.

Effect of the clay fraction on rheological properties

Figs. 9 and 10 contain the variation of the viscosity of Wp and Shp suspensions as a function of the shear rate.

These curves show that, whatever the clay, diluted suspensions exhibit a Newtonian behaviour in the limits of the studied speed gradients¹⁵. This is revealed by a constant viscosity value when the shear rate varies. But for the high diluted suspensions and high shear rates, the viscosity exhibits a moderate increasing.

When the clay percentage increases the rheological behaviour changes and becomes rheofluidifiant. At this state and for the low shear rate values, the viscosity decreases as the shear rate increases. For the high shear rate values, the viscosity becomes constant. The transition between the two behaviour occurs at a clay percentage of 9% (w/w) for the Wp clay and at 10 (w/w) for the Shp one.

These behaviours can be explained by the fact that in the diluted suspensions, the particles are separated and the interparticular interactions are very low. That is why these suspensions exhibit a Newtonian behaviour. Nevertheless, the increase in the viscosity at high shear rates might be due to a new transition order-disorder¹⁶.

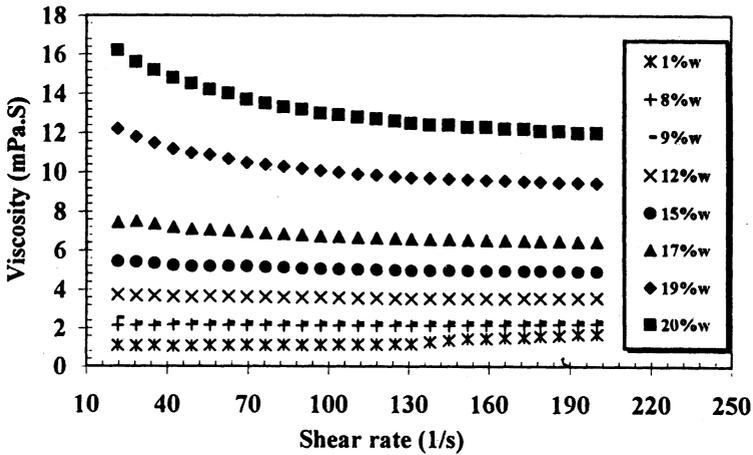


Fig. 9. Effect of Wp clay fraction: Viscosity function of the shear rate

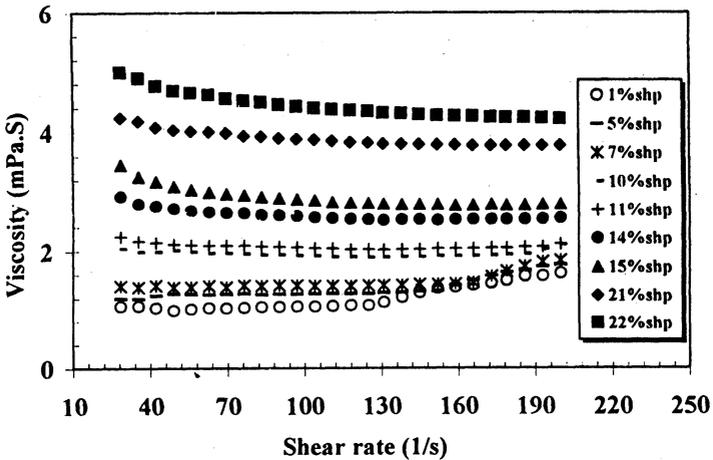


Fig. 10. Effect of Shp clay fraction: Viscosity function of the shear rate

As the clay fraction increases, the density of the suspensions increases and the particles begin to touch each other leading to an increase in the interparticle interactions. This is shown by the transition of the rheological behaviour from Newtonian to rheofluidifiant.

Concerning the concentrated suspensions, the intensity of interparticle interactions increases leading to an increase in the particle's Brownian movement. This occurs particularly at small shear rate by the relatively high viscosity values.

When shear rate increases the reduction in viscosity until a constant value can be attributed to the progressive orientation of the individual platelets in the direction of the flow¹⁷ and by the breaking of the weak edge to edge associations between adjacent platelets which form at low shear stress¹⁸.

Effect of pH on rheological properties

The pH effect on the rheological properties has been studied on the Shp clay at 9% (w/w) and on the Wp clay at 8% (w/w) (Figs. 11 and 12). These curves show that when the pH is weakly acidic or basic (6.13, 8.11 and 8.66 for Shp, and 7.27 and 8.08 for Wp), the suspensions exhibit a Newtonian behaviour characterized by a constant viscosity in the explored range of shear stress. For the basic medium (pH = 9.79 and 10.45 for Shp and pH = 10.67 for Wp), the suspensions exhibit also a Newtonian behaviour but with relatively high viscosity

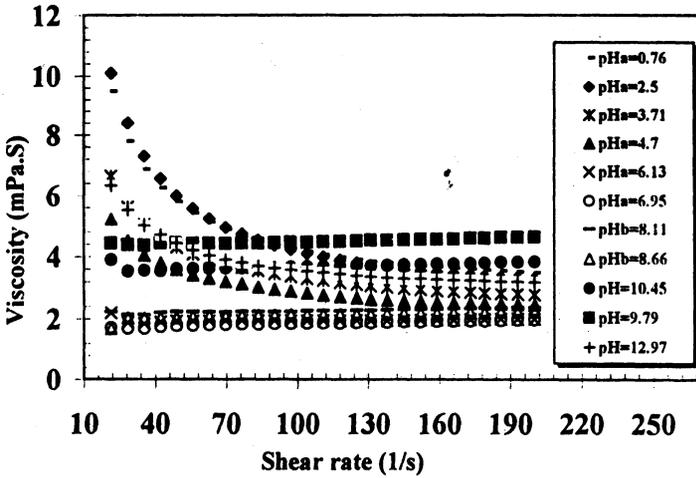


Fig. 11. Effect of pH on Wp suspension : Viscosity function of the shear rate

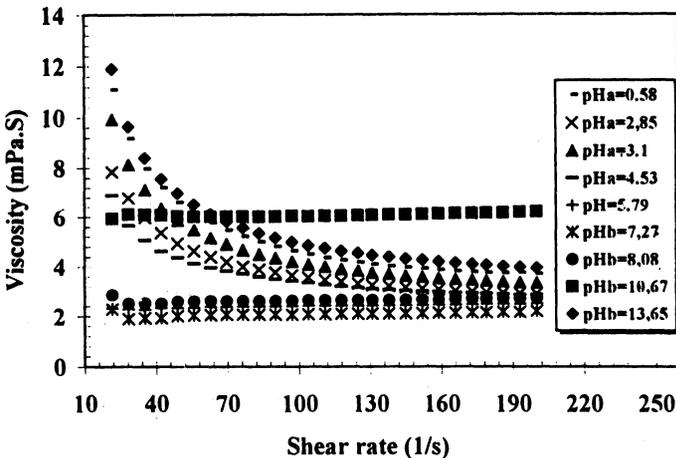


Fig. 12. Effect of pH on Shp suspension : Viscosity function of the shear rate

values. It is interesting to note that these suspensions exist as gel, but flow easily under stress and their reversion in original form is very fast.

For high acidic and basic media (pH = 0.76, 2.5, 3.7, 4.7 and 13.65 for Shp and pH = 0.53, 2.83, 3.10, 4.53, 5.70 and 12.97 for Wp), the rheological behaviour becomes rheofluidifiant. To better understand the pH effect, the evolution of the shear stress as a function of pH has been plotted (Figs. 13 and 14). These curves show two maxima; the first one in acidic medium (pH between 2–4) and the second is in basic medium (pH between 9.5–11). The minimum is around the neutral pH.

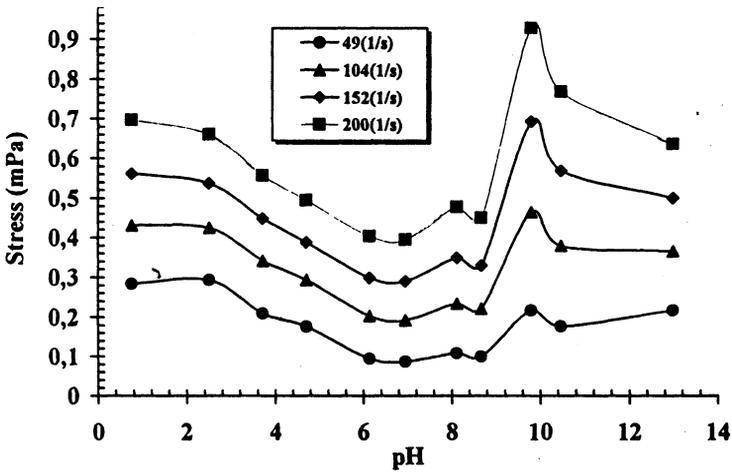


Fig. 13. Wp : Stress function of pH : effect of the shear rate

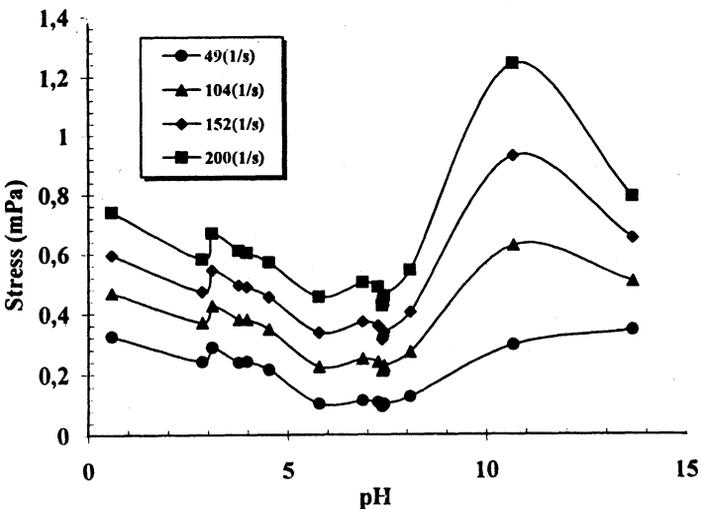


Fig. 14. Shp : Stress function of pH : effect of the shear rate

The interpretation of all these rheological properties variation can be done in terms of interparticular interactions. Indeed, for the neutral pH (suspension of clay in water) the particle interactions are provided by the weak van der Waals' forces (face-to-face interactions); that is why a minimum in the shear stress is observed. When the pH decreases, the edges of clay particles become more and more positively charged and as the faces of particles have a permanent negative charge (due to the isomorphic substitutions), new attractive interactions are created between edges and faces of the clay particles. This explains the rheofluidifiant behaviour observed in acidic media¹⁹⁻²². In strong basic media the rheofluidifiant behaviour can be explained by the fact that (pH > 11), all the edges and all the faces are negatively charged leading to high intensity interparticular repulsions in all directions (edge-to-edge, face-to-face, and face-to-edge).

For the pH values ranging between 9.5 and 11, all the edges are also negatively charged but the value of this charge is lower than that in the strongly basic media, leading to a decrease in the intensity of interparticular repulsions shown by the easy flow of the gel suspensions and the observed Newtonian behaviour. It is interesting to conclude that suspensions in this range of pH, present the rheological properties required for a good drilling fluid leading to explain the pH value of 9-10 used in drilling industry.

Conclusions

The physico-chemical characterization shows that the Jebel-Shemsi bentonite is an interstratified smectite-illite, low-grade kaolinite with quartz and calcite as impurities. According to chemical analysis the smectite represents 80% of the clay fraction and the illite 15%.

The cation exchange capacity of purified Jebel-Shemsi clay is 87 meq/100g and the total specific surface area is 711 m²/g. These two properties are in the same range as that of a smectite.

The rheological properties of the Jebel-Shemsi bentonite are close to those of an industrial Wyoming clay. Indeed, for the effect of clay percentage on the rheological properties, the purified clay suspensions change their behaviour from Newtonian to rheofluidifiant at 10% (w/w) for Shp and at 9% (w/w) for Wp and the values of viscosity are also similar.

Concerning the effect of pH on the rheological properties, it was pointed out that whatever the clay used (Shp or Wp), it exists in two states of maximum interaction in acidic medium (pH range 2-4) and basic medium (pH range 9.5-11). The suspensions corresponding to the first maximum are gels and exhibit a rheofluidifiant behaviour, whereas those corresponding to the second basic maximum are gels; they flow easily and exhibit a Newtonian behaviour. These suspensions exhibit the required rules for a drilling fluid in the pH range (9.5-11) used during drilling operations.

To conclude we can say that the similarity observed between the rheological properties of the Jebel Shemsi bentonite and those of the industrial Wyoming one, gives an opportunity to the Tunisian bentonite to be used in drilling industry if they have suitable filtration properties.

REFERENCES

1. F. Annabi-Bergaya, Organisation de molécules polaires adsorbées par la montmorillonite, Ph.D. Thesis, Université d'Orléans (1978).
2. F. Bergaya and M. Vayer, *Applied Clay Science*, **12**, 275 (1997).
3. J. Beaulie, Identification géotechnique des minéraux argileux naturels par la mesure de leur surface au moyen du bleu de méthylène. Thèse 3^{ème} cycle Univ. Orsay, France (1979).
4. L. Sadok, Caractérisation physico-chimique et étude rhéologique d'argile du bassin de gafsa, D.E.A Faculté des sciences de Bizerte (1998).
5. C. Mauguin, *Bull Soc. Fr. Min.*, **51**, 285 (1928).
6. G. Brown and G.W. Brindley, X-ray procedures for clay mineral indication, 305–395, in: (Eds.), *Crystal Structures of Clay Minerals and their X-ray Identification*, Monograph 5, Mineralogical Society, London (1980).
7. D.M. Moore and R.C. Reynolds, *X-ray Diffraction and the Identification and Analysis of Clay Minerals*, Oxford University Press, Oxford-New York (1989).
8. Reynolds and Hawer, *Clay and Clay Mineral*, **18**, 25 (1970).
9. H. Goboriau, Interstratifiés Smectite-Kaolinite de l'Eure, Relation entre structure, la texture et les propriétés en fonderie, Ph.D. Thesis, Université d'Orléans (1991).
10. R.E. Grim, *Clay Mineralogy*, McGraw-Hill Book Co. Inc, New York (1953).
11. C.S. Calvert, D.A. Palkowsky and D.R. Pevear, A combined X-ray powder diffraction and chemical method for quantitative mineral analysis of geologic samples, in: (Eds.), *Quantitative Mineral Analysis of Clays*, (Eds.), Clay Minerals Society, Bloomington, Indiana (1989).
12. S. Caillere, S. Heniyn and M. Rautureau, *Les argiles*, **Tomes 1 & 2**, Masson (1982).
13. J.B. Dixon and S.B. Weed, *Minerals in soil environments*, Soil Science Society of America, Madison-Wisconsin, U.S.A. (1977).
14. S. Caillere, S. Henin and M. Rautureau, *Les argiles*, *Septima* Paris (1989);
15. M. Moan, Rheological properties of Montmorillonite suspensions, Symposium on Physical Chem. of Interface in Oil Production, St. Raphael, France (September 1992).
16. P. Cousot and H. Van Damme, Physico-chimie et rhéologie des mélanges argileux, Chp. 10, pp. 169–192 (1997).
17. B. Rand, E. Pepenc, J.W. Goodwin and R.W. Smith, *J. Chem. Soc. Faraday Trans.*, **76**, 225 (1980).
18. R. Keren, *Sci. Soc. Am. J.*, **52**, 924 (1988).
19. H. Van Olphen, *J. Colloid Sci.*, **19**, 313 (1964).
20. ———, *Introduction to Clay Colloid Chemistry*, Wiley & Sons, New York, 2nd Edn. (1977).
21. R. Sohm and T.F. Tadros, *J. Colloid and Interf. Sci.*, **132**, 62 (1989).
22. M. Benna, N.K. Ariguib, A. Magnin and F. Bergaya, *J. Colloid Interf. Sci.*, **218**, 442 (1999).

(Received: 27 May 2002; Accepted: 3 March 2003)

AJC-3017