June 2010 ISSN : 0974 - 7486 Volume 6 Issue 2

Trade Science Inc.

Materials Science
An Indian Journal
Full Paper

MSAIJ, 6(2), 2010 [112-119]

Physicochemical characterization and rheological study of Tunisian palygorskite

Mouna Touati*, Memia Benna-Zayani, Hammadi Nciri, Malika Trabelsi Ayadi, Najia Kbir Ariguib
Laboratoire d'Applications de la Chimie aux Substances et Ressources Naturelles et a l'Environnement, Faculte des Sciences de Bizerte, 7021-Zarzouna, Bizerte, (TUNISIA)
E-mail : toumouna@yahoo.fr

Received: 13th February, 2010 ; Accepted: 23rd February, 2010

ABSTRACT

The studied clay is collected from the Tataouine Douiret area of the Tunisian south. The layer contains 50% of clay fraction and 50% of impurities formed essentially from calcite and quartz. The cation exchange capacity (CEC) of purified clay is 43 meq/100g of burnt clay. The physico-chemical characterizations of the clay have shown that it is fibrous clay and particularly it is a palygorskite. The thermal analysis of rough and purified clay has demonstrated that the departure of zeolitic water is carried out at 118°C. The deshydroxylation is occurred at 501°C for the rough palygorskite and at 484°C for the purified palygorskite. The study of the effect of the mass percentage of clay on the rheological properties has shown that the flow curves have Newtonian behaviour for clay fractions lower than 14% (w/w). The effect of NaCl on the rheological behaviour was studied for clay fractions 1.5, 3.25 and 14% (w/w). Concerning the first two clay fractions, the critical flocculation concentration (Ck) is noted at 0.05% of NaCl. For gel (clay 14%), a jump of viscosity is observed from 0.07% of NaCl. From 0.2% of NaCl a very rigid gel is obtained which persists even for high electrolyte percentages.

KEYWORDS

Palygorskite;
Characterizations;
Rheology;
Sol gel transition;
Critical flocculation concentration.

INTRODUCTION

Contrary to common clay minerals, such as smectite, kaolinite, illite, very widespread in Tunisia, fibrous clays and particularly palygorskite few are the information provided on its nature.

The palygorskite is known as "special clay" characterized by fibrous micro morphology and relatively low surface charge[1]. They are silicates aluminous-magnesian in which aluminium and magnesium are in equal proportions with little meadows.

The basic structure of such a clay can be described as being composed of ribbons of phyllosilicate 2:1 which are had even made up of double and triple silicate chains. In fact the ribbons are bound by the inversion of the tetrahedrons SiO_4 through the bands Si-O-Si[2]. Palygorskite characterization was carried out by various studies[3-6]. The fibrous structure of such clay generated a large specific surface, consequently such a clay caused considerable attention in several applications: Adsorption of organic materials, support for catalyses[7], molecular sieve[8] and as an inorganic membrane for ultrafiltration[9]. Moreover because of its special sorption due to its fibrous, colloidal and rheological structure,

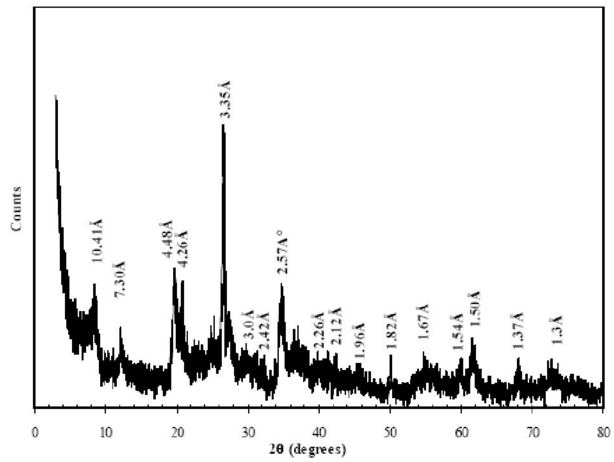

Figure 1 : X-ray diffraction patterns of palygorskite raw powder clay

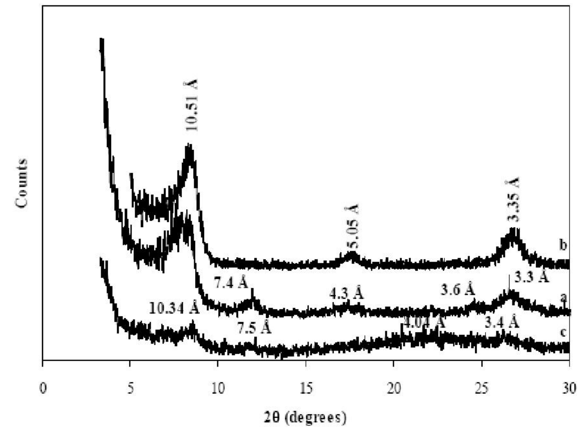

Figure 2 : Diffractogram of the TDp clay oriented on glass slide. (a) air dried oriented slide, (b) heated slide (550°C), (c) ethylene glycol treated slide

the palygorskite has possible industrial and pharmaceutical applications.

The study of the rheological properties of such clay allows optimizing the properties of the clay suspensions to direct them towards other applications. Indeed the rheological properties of the clay suspension can be influenced by some parameters as pH, ionic force, clay fraction[1,10-12].

The variation of clay percentage on the rheological properties leads to locate the sol gel transition. The electrolyte addition on clay suspension affects the ionic force and consequently involves modification in clay suspension behaviour. The palygorskite suspensions behaviour can be explained in a change in particles interactions for various associations (Edge to Face, Face to Face and Edge to Edge). These three models of association are useful to understand the stability and the rheological behaviour of the system clay-water[10-12].

Some authors[1] have studied the effect of electrolyte on plastic viscosity and Bingham yield of Na-palygorskite suspensions at several pH. It was noted that these parameters are slightly affected by electrolyte addition at pH<7 and significantly influenced by electrolyte addition at pH .9.

They explained that for pH<7 the fibres of palygorskite form microagreggates and the addition of electrolytes increases the dynamic viscosity and Bingham yield value by compressing the electrical double layers. At pH>9, the addition of electrolyte to palygorskite suspensions significantly increases the dynamic viscosity and Bingham yield value due to flocculation of the system[1,13,14].

The palygorskite used in our study was collected from the Tataouine Douiret region of the Tunisian south. This study contains two parts; the first one deals with the palygorskite physico-chemical characterization and the second one includes the investigation on the rheological properties of this clay as a function of its percentage and the electrolyte (NaCl) addition in clay suspensions.

EXPERIMENTAL

The characterization was carried out on the raw palygorskite ground and sieved at 100μm and on the purified sodium exchanged clay sieved at 80μm. The raw clay will be noted TDb and TDp for the purified pattern.

The physico-chemical characterization of the clay was carried out by X-ray diffraction (DRX), infra-red spectroscopy, thermal analysis (DTA and TGA), and measurement of cation exchange capacity (CEC) and total specific surface area. Chemical analyses of calcined samples realized at 1000°C was made in the order to evaluate Si, Al, Fe, Mg, Ca, Na, Mn, Ti, P and K oxides content. An atomic absorption spectrophotometer Perkin-Elmer 560 was used for measurements. The X-ray diffraction patterns were obtained using a Philips PW 1710 with α Cu-K radiation. The X-ray diffraction was carried out on powder and 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 spectro-

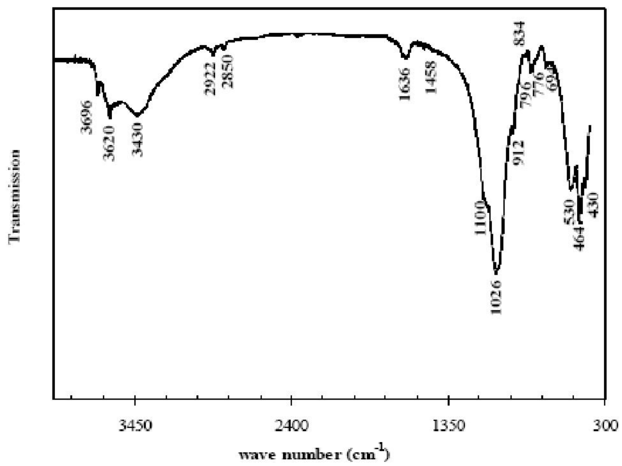

Figure 3(a) : Infrared spectra of the TDb clay

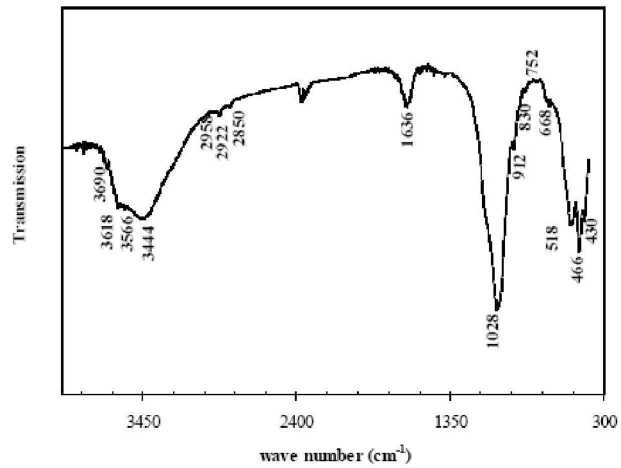

Figure 3(b) : Infrared spectra of the TDp clay

photometer FTIR Perkin-Elmer 1000 in the range 4000-350cm^{-1}. The DTA-TGA were run in a SETARAM TG/DTA 92 apparatus using a sample weight of about 15mg, the heating rate of 10°C/min in Argon, with alumina as reference.

The cation exchange capacities (CEC) were determined by a method which consists in saturating clay with cupric en[15]. The total specific surface area was measured by methylene blue isotherm.

The effect of clay fraction on rheological properties was studied on suspensions prepared by mixing clay powder, at defined quantity, with distilled water. The mixture has been shaken during 24 h then left for three days.

To study the effect of NaCl addition on rheological properties, the suspensions have been prepared by mixing a clay suspension with NaCl aqueous solution during 5 hours then the mixture was left for 3 days. Three clay fractions were used for this aim (1.5, 3.25% and 14% w/w).

The dynamic viscosity and the shear stress were measured on a standard rheometer (Tech Stress Rheometer). The geometry used is coaxial cylinders.

RESULTS AND DISCUSSION

Physico-Chemical characterization

Chemical analysis

Chemical analysis carried out in our laboratory by the reported method[16] and in the present work, the average structural formula of the Na-exchanged purified sample TDp is as:

$(Si_{7.44}\ Al_{0.56})\ (Al_{1.98}\ Fe_{0.87}\ Mg_{0.53}\ Vac_{1.61})\ O_{20}\ (OH)_2\ (OH_2)_4\ Na_{0.22}\ Ca_{0.022}\ Mn_{0.0003}\ K_{0.66}$

This result is comparable with that found by[17].

We note that the clay structure is much related to the nature of the deposit were it was collected.

X-ray diffraction

The X-ray diffraction patterns of TDb (Figure 1) contain:

An intense peak at 10.41Å corresponding to the 110 reflexion of fibrous clay and particularly of palygorskite. Indeed, fibrous nature prevents the orientation according to 001 reflexion.

Two intense peaks at 4.47Å and 4.26Å attributed respectively to 040 and 121 reflexions of a palygorskite[3].

The intense peak at 2.57Å indicates the 161 reflexion of a palygorskite[3].

Two low intense peaks at 7.3Å and 3.5 related respectively to 001 and 002 reflexions of a kaolinite.

Thus the X-ray pattern indicates the presence of a palygorskite containing kaolinite. The impurities are mainly composed of quartz and calcite.

On the TDp air dried oriented slide, heated and treated with ethylene glycol diffractograms (Figure 2) it appears:

An intense peak at 10.51Å on the air dried oriented slide diffractogram (Figure 2(a)); this peak persists even on the two other diffractograms (Figure 3(b) and Figure 3(c)) corresponding to 110 reflexion of palygorskite[3-17,18].

A low intense peak at 3.3Å on the air dried oriented slide diffractogram which persists after heating (Figure

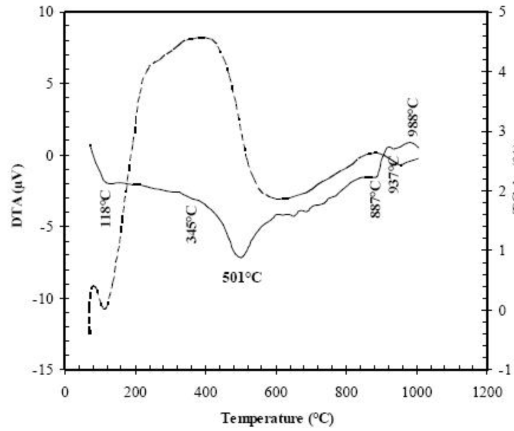

Figure 4(a) : DTA/TG curves of the TDb clay

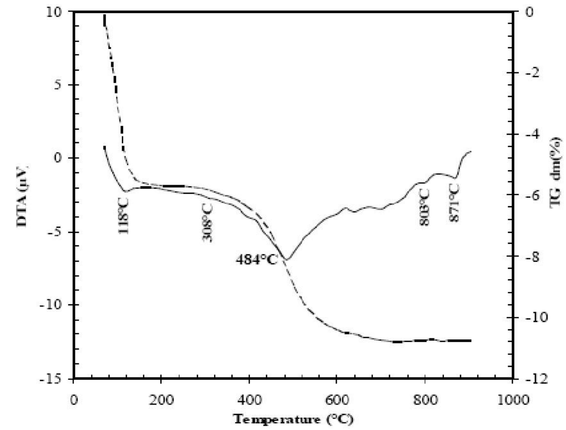

Figure 4(b) : DTA/TG curves of the TDp clay

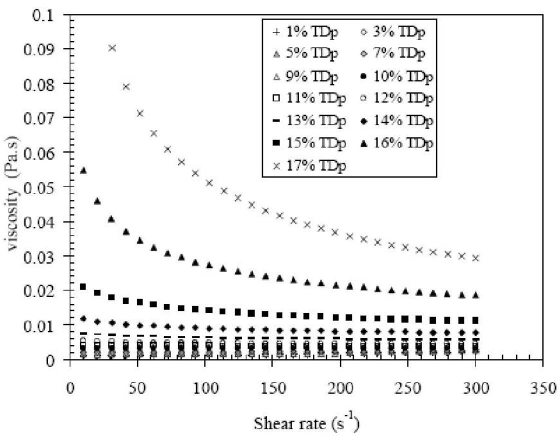

Figure 5 : Effect of TDp clay fraction: Viscosity function of the shear rate

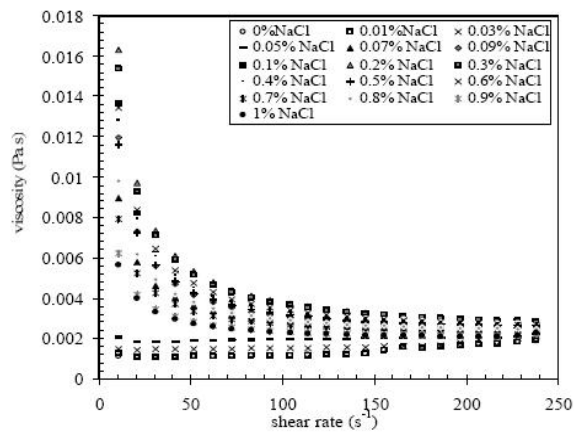

Figure 6 : Effect of NaCl on clay suspension (TDp 1.5%), viscosity function of the shear rate

2(b)). This peak corresponds to 240 reflexion of palygorskite[3].

Two peaks at 7.31Å and 3.6Å which can be attributed to kaolinite, these two peaks disappear after heating which confirm the presence of kaolinite.

With the ethylene glycol treatment (Figure 3(c)), the palygorskite collapse and lost, practically, its fibrous structure, therefore all peaks appears with low intensity.

The X-ray diffraction results permit to conclude that the TD clay is a palygorskite with presence of kaolinite. Few studies have shown that mineral structure of palygorskite change with the Al_2O_3 content[3], and thus with the deposit where it was collected.

Cation exchange capacity and specific surface

One among the fibrous clay properties is the low value of their CEC[19].

The determination of the palygorskite CEC leads to:

The TDb CEC is about 26 meq/100g of calcined clay. After purification this value increases to approximately 43 meq/100g of calcined clay. Indeed, the presence of impurities lowers the CEC value of raw pattern.

The TDp external surface is estimated at 159.6 m^2/g.

Infrared spectroscopy

The IR spectrum of the crude sample (Figure 3(a)) confirms certain results of the X-ray diffraction and brings back other information on the structure of this clay.

Indeed the dioctahedric character of this clay is revealed by Al-Al-OH stretching and bending bands at 3620cm^{-1} and 912cm^{-1}[20,15-21].

The presence of quartz is visualized by the peak to 796cm^{-1}; this peak disappears in the spectrum of the purified sample (Figure 3(b)). A very slight peak at 1458cm^{-1} is relating to the presence of carbonates, this peak practically disappears in the spectrum of TDp clay.

The bands at 3696cm^{-1} (Al-O-H), 1008cm^{-1} (Si-

Full Paper

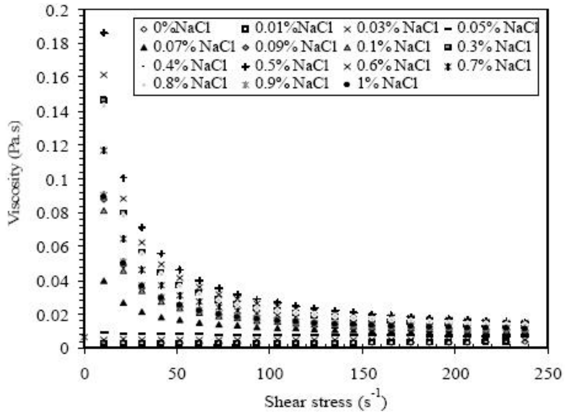

Figure 7 : Effect of NaCl on clay suspension (TDp 3.25%), viscosity function of the shear rate

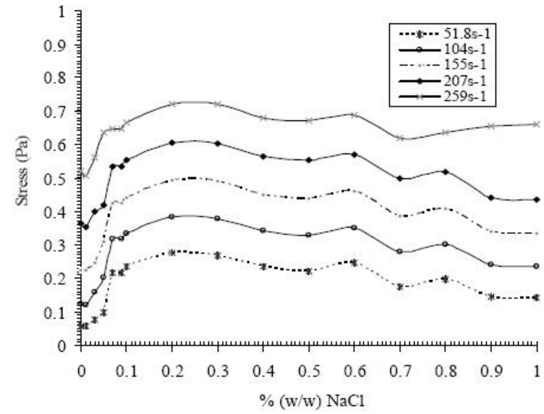

Figure 8 : TDp 1.5%: Stress function of %NaCl: Effect of the shear rate

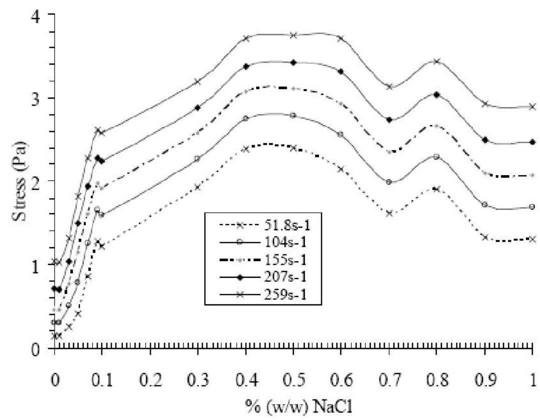

Figure 9 : TDp 3.25%: Stress function of %NaCl: Effect of the shear rate

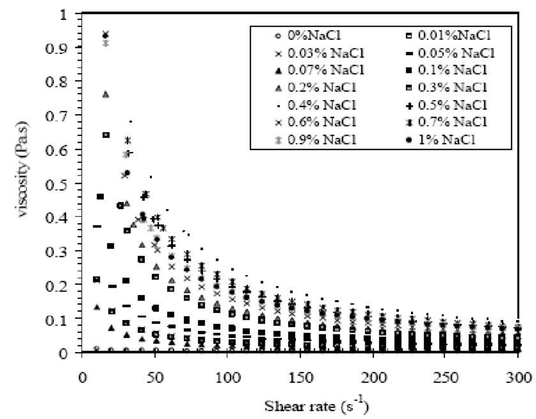

Figure 10 : Effect of NaCl on clay suspension (TDp 7.5%), Viscosity function of the shear rate

O-Al) and 694cm^{-1} (Si-O-Al) signify the presence of kaolinite.

The bands at 3430cm^{-1} and 1636cm^{-1} are characteristic of the vibration of OH water hydration in the clay.

A very weak peak at 3566 cm^{-1} relates to the valence vibration of OH structure.

The bands at 1026cm^{-1} and 434cm^{-1} relate, respectively, to the Si-O-Si valence and deformation vibrations. The Si-O-Al deformation vibration is allotted at 518cm^{-1}. The deformation vibration of Si-O-Mg is located at 466cm^{-1}. The last results attest the existence of octahedral substitution of Al by Mg. This isomorphic substitution is still proven by the presence of a shoulder at 834cm^{-1} relating to the Al-Mg-OH vibration[18].

Thermogravimetric analysis

The DTA and TGA thermograms of the palygorskite clay (Figure 4(a), 4(b)) contain:

A slight shoulder at 118°C may possibly be attenuated by the presence of kaolinite. This shoulder corresponds to the loss of zeolitic water trapped between the ribbons of the clay structure.

A Shoulder at 308°C for the TDp clay corresponding to the loss of crystalline water; according to Callère and Henin[22], Palygorskites show an endothermic pick at 310°C.

Peaks at 501°C and 484°C for TDb and TDp respectively correspond to the clay dehydroxylation.

Two slight endothermic peaks at 887 and 937°C for TDb (Figure 4(a)) which shift to 803°C and 871°C for TDp (Figure 4(b)) this reduction in the temperature can be explained by the impurities departure which tend to raise the transformation temperature.

An exothermic peak is observed at 988°C (Figure 4(a)) that its localization was mentioned in certain studies[3] between 860 and 1045°C. This peak is in linear relation with the Al_2O_3 contents[3].

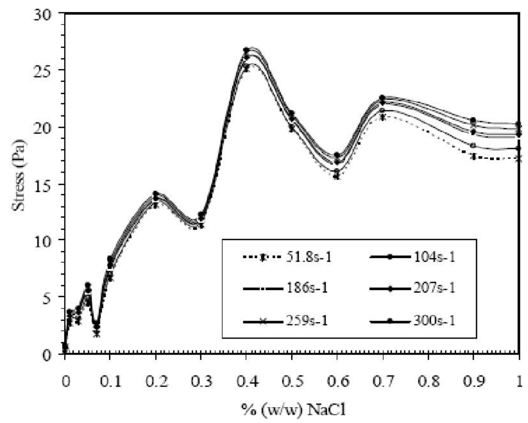

Figure 11 : TDp 7.5%: Stress function of %NaCl: Effect of the shear rate

Rheological properties

The rheological properties were carried out on purified clay TDp. The effect of the clay fraction and the NaCl addition on the rheological properties was studied.

Effect of clay fraction

Figure 5 contains the variation of the viscosity of TDp suspension as a function of the shear rate.

These curves show that diluted suspensions exhibit a Newtonian behaviour. This is revealed by a constant viscosity value when the shear rate varies. However, for the high diluted suspensions, a slight increase in viscosity is noted for high shear rates. When the clay percentage increases the rheological behaviour changes and becomes rheofluidifiant. Indeed, the viscosity decreases as the shear rate increases for the low shear rate value. The viscosity becomes constant for the high shear rate. The transition between the two behaviours occurs at 14% (w/w) for the TDp.

In the case of fibrous clay, particles are an assembly of fiber and then the rheological behaviours are explained according to the fiber arrangement and the length/ width ratio[1]. In our study only the arrangement of fibers in the suspension is cited.

In diluted suspensions, the fibres are largely separated and as the percentage of clay increases the individual fibres of palygorskite are associated into microaggregates[1]. The microaggregates are more voluminous as the clay percentage is higher.

To explain the rheological behaviour of clays the particle term was used by practically all authors. When the suspensions are diluted the particles are largely separated and the interparticular interactions are very low, this explains the Newtonian behaviour observed. As the clay fraction increases, the suspensions become denser and the particles start to be touched leading to an increase in the intensity of interparticular interactions which explain the transition of the rheological behaviour from Newtonian to rheofluidifiant.

For higher clay percentage, suspensions become concentrated; particles are more voluminous and denser, and as shown in figure 5, viscosity values are relatively high for low shear rate value. These observations are due to the increase of the particle's Brownian movement caused by the increase in interparticular interactions. For high shear rate values the suspension viscosity tends towards constant values and this is explained by the orientation of fibres in a flow direction.

Effect of NaCl concentration on sol suspension

The NaCl effect on the rheological properties has been studied on the TDp clay at 1.5% and 3.25% (w/w) (Figure 6 and 7). The curves show a Newtonian behaviour at low NaCl concentration (< 0.05%, 9.0mmol L^{-1}). For the two clay percentages the same behaviour is noted at low shear stress. However, for 1.5% of TDp, more the shear rate increases more viscosity increases while it remains constant for 3.25% of TDp.

It is remarkable to note that we are in the case of sol suspensions that exhibit a Newtonian behaviour and addition of NaCl at low concentration don't affect their rheological behaviour. From 0.05% of NaCl the rheological behaviour becomes rheofluidifiant. To better understand the electrolyte effect, the evolution of the shear stress as a function of NaCl % (w/w) has been plotted (Figure 8 and 9). These curves show a minimum at 0.01% (w/w) corresponding to 0.002 mol.L^{-1} of NaCl. At 0.05% (0.009 mol.L^{-1}) a jump of rheological parameters is observed. Maximums of shear rates are shown from 0.1 to 0.4 % of NaCl at 0.6% and 0.8%, for suspensions at 1.5% TDp. For TDp 3.25%, maximums are shown between 0.4 to 0.6 % and at 0.8% of NaCl.

The indicated results are nearly similar to those found in the case of Na-montmorillonite suspensions and this may be due to the presence of kaolinite.

The effect of the addition of a small quantity of electrolyte causes small compression of the double layer. As result, a small decrease in the studied rheological parameters is observed which explain the minimum at 0.002mol.L^{-1} of NaCl. This result was mentioned in some studies[10,11], it has been noted that the rheological parameters of Na montmorillonite decrease with the addition of weak amounts of NaCl. The minimum in that case was observed at 0.005mol.L^{-1} of NaCl.

For higher NaCl concentrations a jump of viscosity is observed (Figure 6 and 7), the concentration at which this jump begins is known as critical flocculation concentration (Ck). Some authors have located the Ck of 0.025% of Na-montmorillonite suspension in the interval 5-10mmol.L^{-1}[12,23]. According to our study this critical flocculation concentration is located at 9.0mmol.L^{-1}. The increase of viscosity at the Ck value is attributed to an increase of van der Waals attractive forces. As the NaCl concentration increases viscosity is maximal due to the compression of the double layers. By compressing the electrical double layers, electrolyte additions will reduce the absolute value of electrophoretic mobility and finally the microaggregates fall down causing sedimentation of the suspension.

Effect of NaCl concentration on gel suspension

Figure 10 shows the effect of electrolyte addition on the viscosity of suspension corresponding to 14% of clay. In this case the Na-palygorskite exhibits rheofluidifiant behaviour.

As shown, the curves show the same variation for all electrolyte values, the viscosity decreases sharply for low shear rates values then slightly for higher shear rates values. The evolution of the shear stress as a function of NaCl % (w/w) has been, also, plotted (Figs. 11), the figure shows a shoulder at 0.01% of NaCl and a minimum localised at 0.07% of NaCl followed by an abrupt increase of the rheological parameters. Maxima are localised towards (0.2% NaCl, 0.035mol.L^{-1}) and 0.4% of NaCl. For higher electrolyte concentration the rheological parameters are practically constant.

We note that the suspension chosen contains 14% of clay, so we are in the case of concentrated suspension with palygorskite microaggregates. The increase in rheological parameters is due to an increase of attractive van der Waals forces. As the electrolyte concentration increases these parameters rise and finally remain constant for higher electrolyte concentration. Visual observation has shown that from 0.2% of NaCl a rigid gel is obtained which prove that the aggregates stay linked even at high electrolyte concentration. This last result is promising because such clay could be used in drilling mud's.

CONCLUSION

The physico-chemical characterization of Na-palygorskite has been studied and the rheological behaviour of the suspension has been investigated.

The results show that the Tataouin Douiret clay is a palygorskite with presence of kaolinite.

The cation exchange capacity of purified Tunisian palygorskite is 43 meq/100g and the external specific area is 159.6m^2/g, these two properties are in accordance with those of fibrous clay and especially a palygorskite.

Concerning the rheological study, for the effect of the clay percentage on the rheological properties, the purified clay suspensions change their behaviour from Newtonian to rheofluidifiant at 14% (w/w).

The effect of electrolyte on rheological properties of Na-palygorskite suspensions are close to those of swelling clays especially for diluted suspensions. Indeed a minimum of viscosity is detected at 0.01% of NaCl. The critical flocculation concentration Ck, corresponding to a sudden increase of viscosity is detected at 0.05% of NaCl, It corresponded to an increase of the van der Waals attraction forces.

Concerning the gel, the rheological parameters increase as the electrolyte concentration increases. For higher electrolyte concentration there is practically no influence on the rheological parameters. Visual observations have shown that for higher electrolyte concentration a gel is obtained.

REFERENCES

[1] Alexander Neaman, Arieh Singer; Soil Science Society of America Journal, **64**, 427 **(2000)**.

[2] D.A.McKeown, J.E.Post, E.S.Etz; Clay and Clay Minerals, **50**, 667 **(2002)**.

[3] L.Post James; Susan Crawford; Applied Clay Science, **36**, 232 **(2007)**.

[4] M.Suarez, E.García-Romero; Clay and Clay Minerals, **31**, 154 **(2006)**.
[5] E.Mendelovici; Clays and Clay Minerals, **21**, l15 **(1973)**.
[6] Emilio Galan, M.José Mesa, Carlos Sanchez; Applied Clay Science, **9**, 293 **(1994)**.
[7] R.L.Frost, G.A.Cash, J.T.KLopproge; Vibrational Spectroscopy, **16**, 173 **(1998)**.
[8] E.Ruiz-Hitzky; Journal of Materials Chemistry, **11**, 86 **(1997)**.
[9] Q.K.Wang, T.Matsuura, C.Y.Feng, M.R.Weir, C.Detellier, E.Rutadinka, R.L.Van Mao; Journal of Membrane Science, **184**, 153 **(2001)**.
[10] J.S.Chen, J.H.Cushman, P.F.Low; Clays Clay Minerals, **38**, 57 **(1990)**.
[11] T.Permien, G.Lagaly; Clay Minerals, **29**, 751 **(1994)**.
[12] S.Abend, G.Lagaly; Applied Clay Science, **16**, 201 **(2000)**.
[13] W.L.Haden, I.A.Schwint; Ind.Engine.Chem., **59**, 58 **(1967)**.
[14] F.D.Ovcharenko, (Ed.,); The Colloid Chemistry of Palygorskite, Acad.Sci.Ukr. SSR, Kiev, (In Russian), **(1963)**.
[15] F.Bergaya, M.Vayer; Applied Clay Science, **12**, 275 **(1997)**.
[16] M.Touati; Caractérisation Physico-Chimique et etude Rhéologique De La Bentonite De Jebel Stah: Effet de NaCl Sur Les Propriétés Rhéologiques De Cette Argile, D.E.A., Faculté des Sciences de Bizerte, Tunisia, **(2003)**.
[17] S.Chah, A.Petit Decarreau; Clays and Clay Minerals, **50**, 306 **(2002)**.
[18] Yan-Jun Huang, Li.Zhen, Li.Shu-Zhen, Zi-Liang Shi, Lin Yin, Yuan-Fu Hsia; Nuclear Instruments and Methods in Physics Research, **260**, 657 **(2007)**.
[19] S.Callere, S.Henin; Mineralogical Society, 231 **(1957)**.
[20] J.Beaulie; Identification Geotechnique Des Minéraux Argileux Naturels Par La Mesure Des Leur Surface Au Moyen Du Bleu De Méthylène, Thesis, University of Orsay, France, **(1979)**.
[21] E.A.Lvarez-Ayuso, A.Garcia-Sanchez; Journal of Hazardous Materials, **147**, 594 **(2007)**.
[22] S.Caillère, S.Hénin, M.Rautureau; Minéralogie Des Argiles, Tomes 1 et 2, Masson, 184-189 **(1982)**.
[23] D.Penner, J.Lagaly; Clay and Clay Minerals, **48**, 246 **(2000)**.