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Correlation between rheological and filtration properties of clay suspensions

Mémia Benna-Zayani*, Hammadi Nciri, Mouna Touati, Lobna Jerbi,
Malika Trabelsi Ayadi, Najia Kbir Ariguib
Laboratoire d'Applications de la Chimie aux Substances et Ressources Naturelles et à l'Environnement
Faculté des Sciences de Bizerte,7021 Zarzouna, Bizerte, (TUNISIA)
E-mail : memia.benna@fsb.rnu.tn, memiabenna@yahoo.fr

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ABSTRACT

In order to correlate rheological and filtration parameters of clay-aqueous suspensions, the effect of acidic pH and ionic strength have been investigated. Two clays, a bentonite and a palygorskite were used to emphasize the contribution of the nature of the clay. Rheological results show that at a given bentonite percentage, when the pH of the suspension decreases, the yield stress and dynamic viscosity increase and reach a maximum at weakly acidic media before decreasing again in highly acidic medium where the structure of the clay is probably attacked. The NaCl addition to palygorskite suspensions causes an abrupt increase in viscosity at the critical flocculation concentration (CFC) revealing the beginning of the flocculation. When the ionic strength increases further, the viscosity reaches a maximum then decreases when the suspension becomes unstable. The effect of the pH on the filtration properties for the bentonite appears to be the same as on the rheological properties. When the pH decreases, the thickness (e), the weight (m) and the water retention (WR) of the cake increase, reach a maximum for weakly acidic pH before decreasing again. The permeability of the cake increases below the pH corresponding to the observed maximum for the other filtration parameters. However, the addition of NaCl and the flocculation phenomenon seem to have no effect on the filtration properties of the palygorskite. There is no correlation between rheological and filtration parameters for the non swelling and fibrous clay.

KEYWORDS

Rheology;
Static filtration;
Bentonite;
Palygorskite;
Correlation.

INTRODUCTION

Sol-gel transition and changes in rheological behaviour of clay-water systems can be observed in many industrial applications as well as under natural conditions. Theses complex phenomena depend on many factors such as the nature of the clay, the pH and the salinity of the suspending water[1-14].

Particularly, the use of clays in drilling fluids is based on their ability to present specific rheological and filtration properties under dynamic and static conditions. In this context, the objective of the present study is to show the existence or not of correlation between rheological and filtration properties of two clays: a lamellar and swelling purified bentonite and a non swelling and fibrous purified palygorskite.

EXPERIMENTAL

Materials

The bentonite used in this study is from western-south of Tunisia and precisely from the region of Berka near the town of Gafsa. This bentonite was at first purified by the classical NaCl exchange[15-17]. This purified clay fraction is a dioctahedral interstratified smectite-illite containing 78% of smectite and 20% of illite with a smaller amount of free kaolinite (~2%). Its dioctahedral smectite fraction has a pronounced montmorillonitic character. It's Cation exchange capacity (CEC) is equal to 101.9 meq/100 g of calcinated clay and its total specific surface area is equal to 735,9 m^2 g^{-1}. This later propriety is very important since it indicates the ability of the clay to swell. Its average structural formula is:

$(Si_{7.653}Al_{0.348})^{IV}(Al_{2.775}Fe_{0.614}Mg_{0.565}Ti_{0.033}Mn_{0.001})^{VI}O_{20}(OH)_4$
$Na_{0.623}Ca_{0.017}K_{0.259}$

The purified bentonite will be noted "BP".

The palygorskite clay is from eastern-south of Tunisia and precisely from the region of Douiret near the town of Tataouin. This palygorskite was at first purified as the bentonite. The purified palygorskite contains a small amount of kaolinite (~5%). It's Cation exchange capacity (CEC) is equal to 43 meq/100 g of calcinated clay and its average structural formula is:

$(Si_{7,4424}Al_{0,5575})(Al_{1,9827}Fe_{0,8749}Mg_{0,5262}Vac_{1,6161})O_{20}(OH)_2(OH_2)_4$
$Na_{0,2237}Ca_{0,0222}Mn_{0,0003}K_{0,6627}$

The purified palygorskite will be noted "Tap".

All the samples were prepared by using the same method, to take account of the great influence of particle grain size and of the method of preparation on the final state of suspensions (the degree of dispersity) and thus, on the rheological and filtration properties. The dry purified clay powder was first sieved to 80μm size. Care was particularly taken to prevent an attack of the clay structure by avoiding direct contact of acidic solutions with the dry clay powder. The purified clay was previously mixed with distilled water, mechanically shacked (160rpm) for 5 hours and left at rest for 14 hours. Then the acidic (HCl) or electrolyte (NaCl) solution (50% by weight of the final suspension) was added to the clay aqueous suspension. The mixture was finally mechanically shacked (160rpm) for 5 hours and left at rest for 24 hours before experiments.

TABLE 1: The tested percentages of clays

% BP	1	3	4	5	6	7	8.5	9.5	11	12
% Tap	1	3	5	7	9	10	11	12	13	14
% Tap	15	16	17							

TABLE 2: The tested percentages of NaCl and concentrations of HCl

C_{HCl} (mol L^{-1})	% NaCl (w/w)	% NaCl (w/w)	% NaCl (w/w)
0	0	0.05	0.6
10^{-5}	0.005	0.06	0.7
10^{-4}	0.01	0.07	0.8
10^{-3}	0.015	0.08	0.9
10^{-2}	0.02	0.09	1
10^{-2}	0.025	0.1	-
10^{-1}	0.03	0.2	-
-	0.035	0.3	-
-	0.04	0.4	-
-	0.045	0.5	-

The sodium chloride NaCl (99.8%) and chlorhydric acid (HCl) were provided by Prolabo.

The tested percentages of clays are summarized in TABLE 1 and the percentages of NaCl and concentrations of HCl used are grouped in TABLE 2.

The conversion of percentages (w/w) of NaCl to molar concentrations and then to ionic strength is given by the following formula:

$$\mathbf{I = C_{NaCl}(mmol.L^{-1}) = \frac{1000y}{(58.5(1000-x-y)}} \qquad (1)$$

where << x >> is the percentage (w/w) of clay and << y >>is that of NaCl in the suspension.

Rheological measurements

The rheological measurements were performed using a Tech Stress Rheometer which operates in a rate-controlled mode. The rheometer is connected to a computer which records the data. A Software Tech Stress was used.

For steady state measurements, a Couette geometry was used for liquid suspensions with a gap of 2 mm (the internal radius is 25 mm and the external one is 27 mm). The volume of the suspension to test is equal to 16 mL. For the gel state suspensions, a cone plate geometry (C40 4) was used with a radius of 20 mm and an angle of 4°.

During the rheometrical measurements, viscosity and shear stress were read in the range of shear rate [0.1, 300 s^{-1}].

For yield stress measurements, the vane method was used (H= 19 mm and D = 10 mm).

Static filtration

The suspensions were filtered in a stainless steel Millipore filtration cell and the constant pressure was obtained with compressed air. The filtrate volume was followed as a function of time. The final filtrate's volume is then notes (V_{ff}).

The water retention is defined as:

$$WR = 100\ (1 - \frac{V_{ff}}{V_{iw}}) \qquad (2)$$

where "V_{iw}" is the volume of water in the initial clay suspension.

Static filtration experiments were carried out on 20 mL of clay suspension under 1.5 bar (1.5 10^5 Pa) and 5.7 bar (5.7 10^5 Pa). At the end of filtration, the cake was removed from the filtration cell and immediately weighted and its thickness was measured using a calliper.

The coefficient of permeability (k) is expressed in square meters and represents a cross-section of flow. "k", was calculated assuming that the microstructure of the cake is homogeneous[18-23] which means that k is constant and derived from the Darcy law:

$$\frac{dV_{tf}}{dt} = \frac{k\,S\,P}{\mu\,e} \qquad (3)$$

where "V_{tf}" is the filtrate volume (m^3) at time t, "S" is the filtration surface (m^2), here S = 13.2 10^{-4} m^2, "P" is the applied pressure (Pa), "μ" the filtrate viscosity (Pa s), in our experiments μ =1 mPa s = viscosity of water, and "e" is the thickness of the cake (m).

All calculations were made in previous works[16,21,22]. The final form of the Darcy law can be written as follows:

$$V_{tf}^{\ 2} = \frac{2\,k\,S\,P}{\mu\,e} V_{ff}\ t \qquad (4)$$

Thus, the permeability, k, can be determined experimentally from $V_{tf}^{\ 2}$ = f(t) plots, where the linear slope is equal to $\frac{2\,k\,S\,P\,V_{ff}}{\mu\,e}$

RESULTS AND DISCUSSION

Effect of pH on rheological and filtration properties

The effect of pH on rheological and filtration properties has been studied only on the "BP" bentonite

The variation of the yield stress and the dynamic viscosity as a function of pH at a fixed percentage of clay (8.5% BP) is shown in figure 1. Starting from the natural pH value (pH = 7.65), the yield stress and the dynamic viscosity increase as the pH decreases, reaches a maximum, and after this they decreases at high acidic medium.

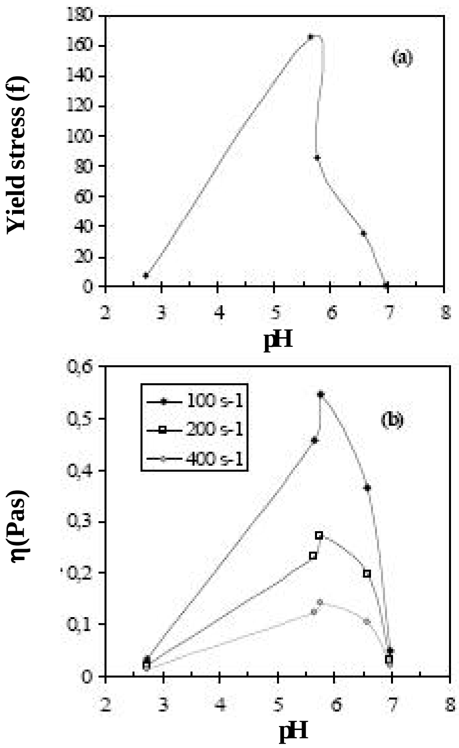

Figure 1: Variation of the yield stress and dynamic viscosity as a function of the pH 8.5% BP

The same variation is observed for the filter macroscopic parameters, according to the pH of the initial clay suspension. In deed, as shown in figure 2, the thickness, the weight and the water retention of the filter cake pass through a maximum in moderate acidic pH. The permeability in turn, its magnitude remains fairly constant and increasing significantly from the pH at which the rheological parameters decrease.

This can be explained by the fact that at pH values less than the isoelectric point, all the edges are positively charged, which makes the edge-to-face interactions possible and the mechanism by which the three-dimensional network is formed in the gel could be the connection between edges and faces (card-house structure)[22]. That is why an increase of the yield stress and thickness, weight and water retention of the cake is observed. At very high acidic medium, the ionic strength is very high and the double layers are very compressed; this reduces the dominance of the edge-to-face

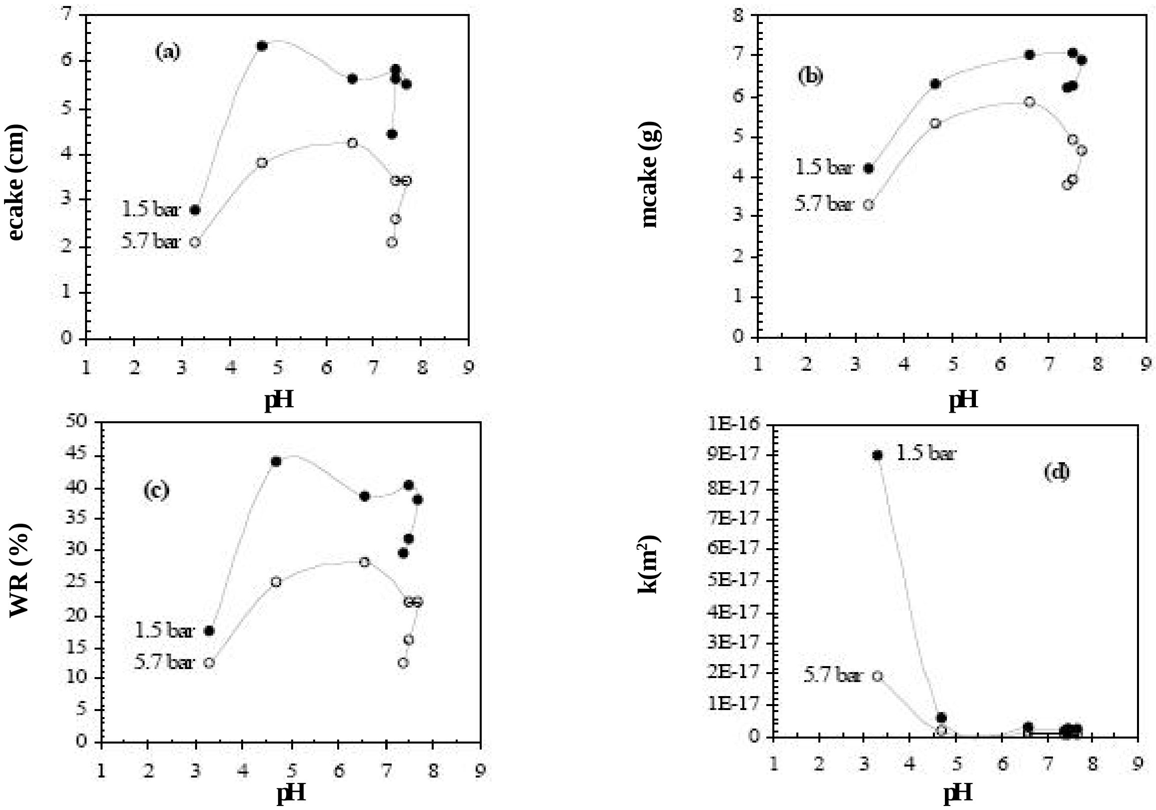

Figure 2: Variation of the thickness, the weight, the water retention and the permeability of the filter cake as a function of the pH 8.5% BP

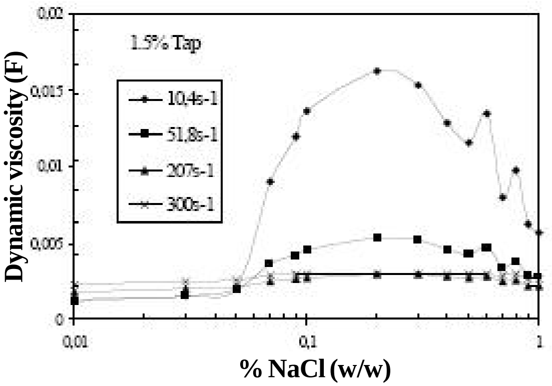

Figure 3: Variation of the dynamic viscosity as a function of the percentage of NaCl. 1.5% Tap

attraction and leads to the breakdown of the card-house structure. Moreover, in this range of pH the structure of the clay is probably attacked by the protons, that is why the yield stress decreases at strongly acid medium. This is confirmed by the increase of the cake's permeability.

In addition, visual observation has shown that gels obtained at acidic pH (when the yield stress reaches its maximum) are opaque. This observation may be connected to an aggregated structure with particles in contact, which means the dominance of attractive interparticular forces. Moreover, we noticed at very high acidic medium the existence of a thin film of water at the surface of the sample, which indicates sedimentation of aggregates that are probably partially attacked in the very high acidic condition.

Effect of ionic strength on rheological and filtration properties

The effect of the ionic strength, by NaCl addition, on rheological and filtration properties has been studied only on the "Tap" palygorskite.

The variation of the dynamic viscosity as a function of NaCl percentage in the clay suspension allows the detection of the critical flocculation concentration (CFC) which is the first concentration of NaCl (ionic strength) at which the phenomenon of flocculation begins.

Results show, for 1.5% (w/w) of Tap clay, a sudden rise of dynamic viscosity at a percentage of NaCl equal to 0.05% of NaCl ($I = 0.856$ mmol L^{-1}) corresponding to the CFC and a maximum at 0.2% of NaCl ($I = 3.42$

mmol L^{-1}) beyond which the suspension becomes unstable and sediments (figure 3). The same results are also found for 3.25% of Tap clay for which the CFC happens at 0.05% of NaCl (I = 0.857 mmol. L^{-1}) and the maximum is observed at 0.4% of NaCl (I = 6.86 mmol L^{-1}) (figure 4).

In absence of NaCl, diluted suspensions have a Newtonian behaviour, the particles are dispersed and the forces between their electrical double layers are repulsive (F-F). The addition of NaCl causes the compression of the double layers and the decrease of intensities of electrostatic repulsion forces. At this stage, the attractive Van Der Waals forces between clay particles (Face-to-Face (F-F), but also Face-to-Edge (F-E) and Edge -to-Edge (E-E)) begin to increase and then to contribute in the total interparticular interactions. And when these attractive interactions become dominant, the flocculation is generated. This phenomenon of flocculation is detected by a considerable increase in the rheological parameters.

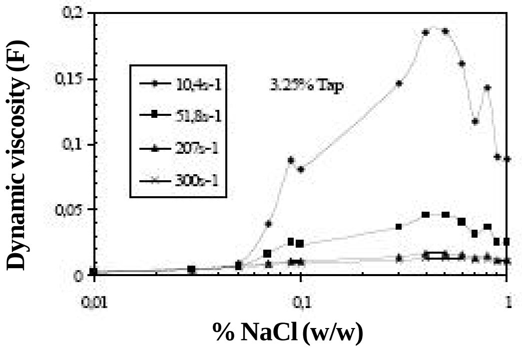

Figure 4: Variation of the dynamic viscosity as a function of the percentage of NaCl. 3.25% Tap

For higher amount of NaCl, double layers are so compressed that the voluminous clay particles are so contracted and therefore some of the interparticular links are broken causing sedimentation which is visually easy to detect. Indeed, during experiments, sedimentation began at 0.2% and at 0.4% of NaCl for respectively 1.5% and 3.25% of Tap. It is important to note that the layer of water surmounting the sediment increases with NaCl concentration.

The results of static filtrations of the palygorskite suspensions under two different pressures (figures 5 and 6) do not show any systematic correlation between rheological properties and filtration properties. Indeed, at 1.5 % and 3.25 % of Tap, the variation of the thickness of the filter cake, its weight and its water retention shows no particular point that could detect the onset of flocculation (CFC) or the beginning of the instability of suspensions. However, the variation of permeability shows, at 1.5% Tap, an abrupt increase at the percentage of NaCl corresponding to the CFC. At

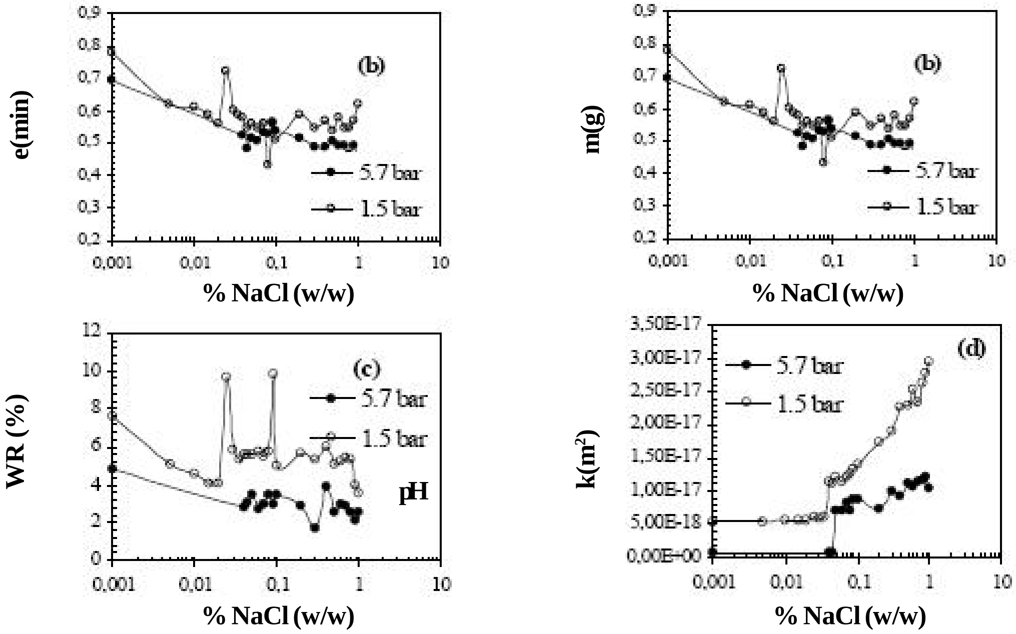

Figure 5: Variation of the thickness, the weight, the water retention and the permeability of the filter cake as a function of the NaCl percentage. 1.5% Tap

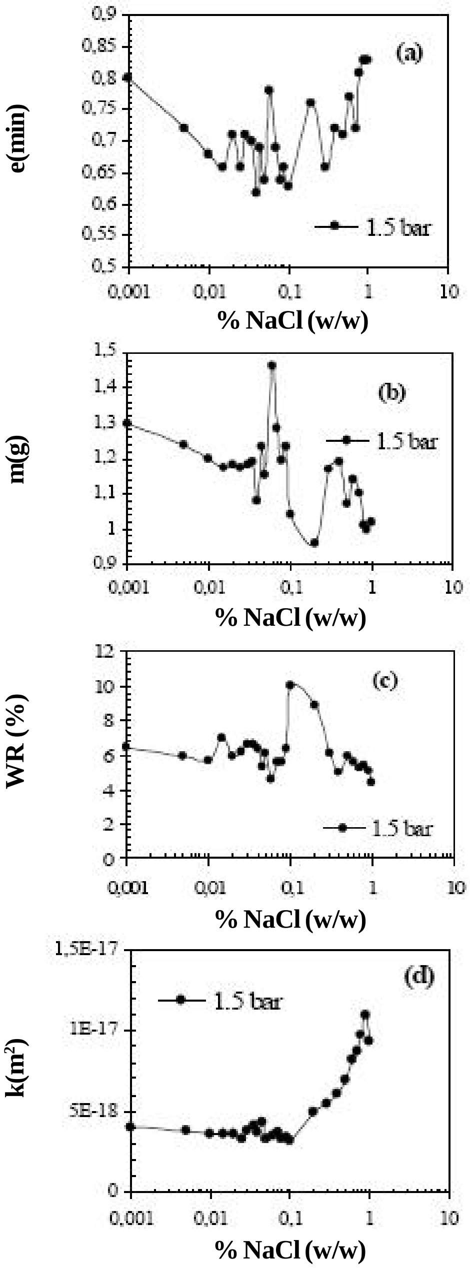

Figure 6: Variation of the thickness, the weight, the water retention and the permeability of the filter cake as a function of the NaCl percentage. 3.25% Tap

3.25% Tap an increase of the permeability is also detected but at a percentage of NaCl which corresponds neither to CFC nor at the beginning of instability of clay suspensions.

Salt addition changes the balance between repulsive and attractive forces among clay particles, which will have several consequences. Indeed, with increasing ionic strength, as the system has an identical amount of clay particles before and after flocculation, the changes can only be due to a change in the nature of interparticular interactions. The rheological parameters are highly dependent on the NaCl concentration, whereas the filtration parameters of the palygorskite clay seem to be independent on NaCl concentration. The absence of any correlation between rheological properties and filtration properties is probably due to the fibrous morphology of palygorskite particles and their rigidity compared to those of swelling clay. Pantet et al.,[24] have found the same results when studying the filtration properties of a kaolinite clay which is also non swelling clay[24].

CONCLUSION

The aggregation of clay particles by means of pH and salinity variations has been investigated on a bentonite and a palygorskite respectively.

The results show a good correlation between the rheological properties, which are highly dependent on the changes in interparticular interactions in clay suspensions, and the filtration properties for the bentonite clay. Whereas the structural parameters of the filter cake obtained with palygorskite clay suspensions seem to be independent of any change in interparticular interaction in the initial suspension and this regardless of the applied pressure. There is no correlation between rheological and filtration parameters for the fibrous and non swelling palygorskite.

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