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Valorization of mixed metal hydroxide on Algerian Na-Bentonite suspensions: Application to water-based drilling fluid

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ABSTRACT

The use of mixed metal hydroxide tri-cationic (Li^+ , Mg^{+2} , Al^{+3}) in water based drilling fluids brought to the birth of a new air and perspective to improve the using of Bentonitic suspension as viscosifier in drilling fluids.

The aim of this work is to study the possibility of using mixed metal hydroxide and see his effect at different percent (5%, 10%, 15% and 20% by Wt of Bentonite) on the rheological behavior and colloidal properties of Algerian Na-Bentonite suspension (30 kg/m^3).

Rheological tests and Zeta Potential measurements have been performed for each prepared suspension. The results show that the adding of MMH on Algerian Na-Bentonite increases the yield stress to 1.39 Pas at 20% MMH, however a stable suspension was observed -41 mV of Zeta Potential measurement at 10% MMH with yield stress of 1.17 Pas.

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1. Introduction

Introduction of mixed metal hydroxide (MMH) to the drilling fluids industry need to develop understanding of the mechanism by which such fluids operate and methods by which may be applied to maximum advantages [1]. By addition of mixed metal hydroxides, typical Bentonite muds are transformed to an extremely shear-thinning fluid [2]. The shear thinning rheology of mixed metal hydroxides and Bentonite fluids is due to the formation of a three-dimensional, fragile network of mixed metal hydroxides and Bentonite. The positively charged, mixed metal hydroxide particles attach themselves to the surface of negatively charged Bentonite platelets. Typically, magnesium aluminium hydroxide salts are used as mixed metal hydroxides [3].

Following many advantages of mixed metal hydroxide drilling mud has been used successfully in horizontal wells; in tunnelling under rivers, roads, and bays; for drilling in fluids; for drilling large-diameter holes; with coiled tubing; and to ream out cemented pipe [4]. Mixed metal hydroxides can be prepared from the corresponding chlorides by treatment with ammonia [5]. Experiments with various drilling fluids showed that the mixed metal

hydroxides system, coupled with propylene glycol [6], caused the least skin damage of the drilling fluids tested. Thermally activated mixed metal hydroxides, made from naturally occurring minerals, especially hydrotalcites, may contain small or trace amounts of metal impurities besides the magnesium and aluminium components, which are particularly useful for activation [7]. Mixed hydroxides of bivalent and trivalent metals with a three-dimensional spaced-lattice structure of the garnet type ($\text{Ca}_3\text{Al}_2[\text{OH}]_{12}$) have been described [8,9,10].

Starting with characterization of used materials such as Na-Bentonite and MMH, the preparation of the suspensions until having a satisfactory result intended for the water-based drilling fluid. The first step, rheological behaviour study for different suspensions have been established using AR2000 Rheometer. According to the rheological results all Rheogram obtained describe a Shear-thinning behaviour of the **Hershel-Buckley** model.

Other side, suspension stability study has been performed by Zetameter 2000 Instrument for each prepared suspension. The Adding of MMH on Na-Bentonite suspension (30 kg/m^3) improves the colloidal stability and the optimal result was recorded at 10% MMH.

2. Materials and methods

The materials used in this work summarized in: mixed metal hydroxide, Na-Bentonite, Soda Ash and Caustic Soda.

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2.1. Characterization of the used materials

2.1.1. Mixed metal hydroxide (MMH) characterization:

The mono-dispersed mixed metal layered hydroxide has the empiric formula $\text{Li}_m\text{D}_d\text{T}(\text{OH})_{(m+2d+3+na)}\text{A}_a^{\text{n}}\cdot\text{H}_2\text{O}$ where:

D: is divalent metal such as Mg.

T: is Trivalent Metal such as Al.

A: represents other monovalent or polyvalent anions [11,12,13].

2.1.1.1. Chemical composition. Table 1 represents the chemical composition of MMH; According to obtained results we found that Magnesium and Lithium ions represent 60% and Layered hydroxide of Aluminium 40%. The presence of Mg^{+2} and Al^{+3} improve rheological properties of Bentonite suspension by creating 3D layers Network.

2.1.1.2. Physical and chemical properties. Physical properties of MMH in Table 2 show a good Acid dissolution 90%, this property allowed using it as reservoir friendly product and the alkalinity

Table 1
Chemical composition of MMH.

Chemical Name	Percent
Layered hydroxide of Aluminium	40%
Magnesium and Lithium ions	60%

Table 2
Physical composition of MMH.

Properties	Description/Values
Physical State	Solid
Moisture	09.5%
Acid dissolution	90%
PH	9.5
Specific Gravity/Density	0.95

Table 3
Conformity test results of Na-Bentonite.

Parameters	Requirements values	Measured values
Moisture	10% Max	10%
Reading 600 tr/min	22 Min	26
Yp (lbs./100ft ²)	3xPV Max	PV = 12 Cp, Yp = 25 lbs/100ft ²
Filtrate (ml)	15 ml Max	11 ml
pH	9.5 Max	9.4

property (ph. = 9.5) provide a good environment for Bentonite hydration and polymers performance.

2.1.2. Na-Bentonite characterization

The Bentonite used in this work is an Algerian Na-Bentonite. This Bentonite was characterized before being used as following:

2.1.2.1. Conformity test. All Bentonite destined for drilling fluids must meet certain requirements. The conformity test is carried out according to API 13A SEC 4: a suspension of 22.5 g of Bentonite dissolved in 350 ml of distilled water and monitored for 24 h at a temperature of 16 °C. The test is done with Viscometer FANN 35A [14].

According to results in Table 3, found that Yp value was not respected the requirement (Yp = 25 lbs/100 ft², indeed 36 lbs/100 ft²). So, conclude that the current Na-Bentonite is not complies with API 13A. For that, the improvement of swelling properties of Na-Bentonite is primordial. The adding of MMH considered as one of solutions to improve swelling properties of Na-Bentonite.

2.1.2.1.1. Mineralogical composition. According to XRD results of Fig. 1, the Montmorillonite is a dominant clay mineral (82%) result that Na-Bentonite is Montmorillonite type. It has been identified around 15° A. The resulting spectrum shows that the clay also contains impurities in the form of quartz.

2.1.2.1.2. Chemical composition. According to Table 4, the dominance of the silica and alumina in the composition represents the Montmorillonite mineral in Bentonite and their percentage improves the swelling characteristics.

2.2. Suspensions preparation

2.2.1. Na-Bentonite suspension

In a graduated cylinder, measure the required amount of fresh water and transfer to Hamilton Beach-mixer with three speeds. Add a required amount of soda Ash to treat the hardness of used water, following by the required quantity of Bentonite gradually than mix well at high speed for 20 min. Allow the Bentonitic suspension to rest for a minimum of 6 h to obtain a good pre-hydration.

2.2.2. MMH/Na-Bentonite suspensions

Take the prepared pre-hydrated Bentonite slurry and gently add the required amount of MMH than mix for 10 min with a medium speed, during the mixing scraping the walls of Boule.

Adjust pH = 10 with caustic soda.

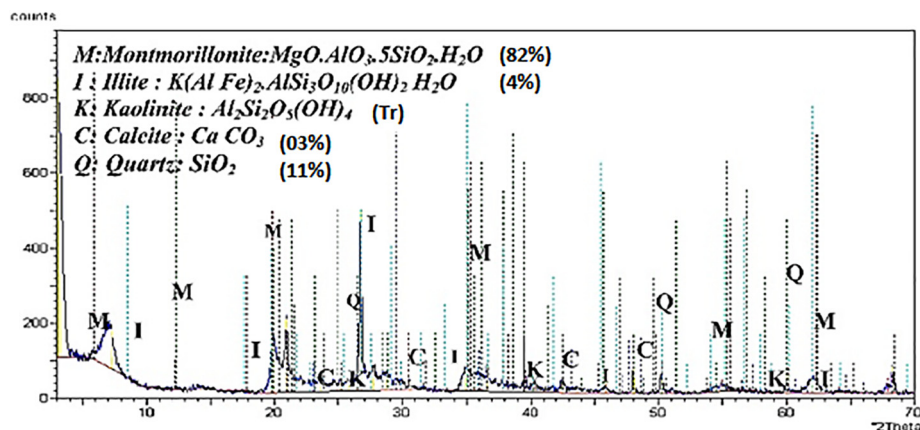


Fig. 1. XRD Diffractogram of Na-Bentonite.

Table 4
Chemical composition of Na-Bentonite.

Oxydes	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	Na ₂ O	K ₂ O	MgO	CaO	MnO	LO.I/1100 °C
%	46,1	18,0	1,62	1,19	0,65	0,87	–	0,16	28,00

2.3. Test procedures

2.3.1. Rheological test of the suspensions

All the rheological measurements were carried out using an imposed stress rheometer (AR 2000) at a temperature kept constant at 30° C (Consider as the ambient temperature in the south region of Algeria as Ain Salah) using geometry of cone-plane for solutions of polymers and polymer fluids, the choice of the diameter of the cone and its angle depend on the experimental conditions and the viscosity of the material, the sample is placed between a cone of defined radius 60 mm and an angle of 2° and a flat surface perpendicular to the axis of the cone. In order to avoid evaporation during handling, the measuring device was placed in an atmosphere saturated with water vapour.

2.3.2. Zeta potential

Take an amount of each prepared suspension with a concentration of 01 g/l and pass the sample into the Zeta-Sizer 2000 cell for test Zeta Potential.

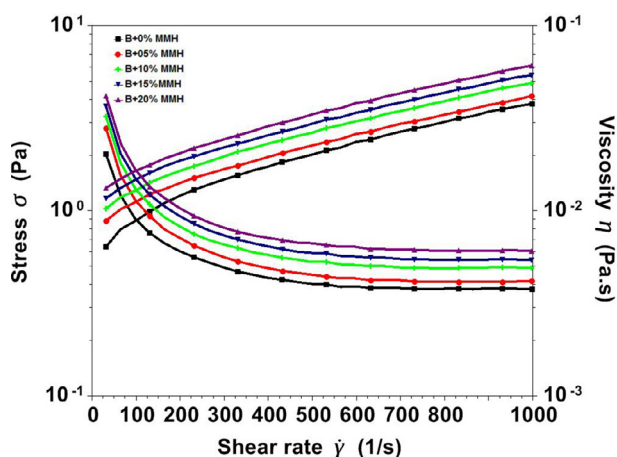


Fig. 2. Rheogram of Na-Bentonite suspension/MMH.

3. Results and discussion

3.1. Rheology measurements of suspension Algerian-Na bentonite/MMH

Many experimental studies have shown that the rheological behaviour of water-clay suspensions, particularly drilling fluids, can be described by a Herschel-Bulkley model [15,16].

In Fig. 2, the effect of the presence of the mixed metal hydroxide on the rheological behaviour of the Na-Bentonite suspension can be observed. According to Rheogram, the viscosity and the shear stresses increased with addition of MMH (of 0%, 5%, 10%, 15% and 20%) on Na-Bentonite (30 kg/m³). All the flow curves obtained can be described by the Herschel-Bulkley model with a low yield stress, in particular for the suspension of basic Na-Bentonite (0.70 Pas at 0% MMH) and the Na-Bentonite-MMH mixture. Note also the drastic increase of all the rheological properties of the Na-Bentonite suspension (including the yield stress) obtained with the addition of the MMH (1.39 Pas at 20% MMH) [17].

When Na-Bentonite and MMH are dispersed together in water, the highly positive MMH crystals migrate and attach to the negative sites on the basal planes of the Bentonite platelets. The new complex produces slurry having quite unusual rheological and suspension characteristics. For all Na-Bentonite-MMH mixtures, a change in curvature is observed for all of the flow curves in the region at low shear rates. This indicates that the Na-Bentonite-MMH system has a threshold stress. It is also observed that the value of the threshold stress increases with the increase in the concentration of MMH. Note that the dependence between shear stress and shear rate is not strong enough. This is in agreement with the results of conducted on similar mixtures [18].

These results are more visible when the Rheogram are drawn as the variation of the apparent viscosity as a function of the shear rate in Fig. 2. For each mixture, two regions are observed:

1. The existence of the yield stress and decrease in viscosity in a small range of low shear rate.

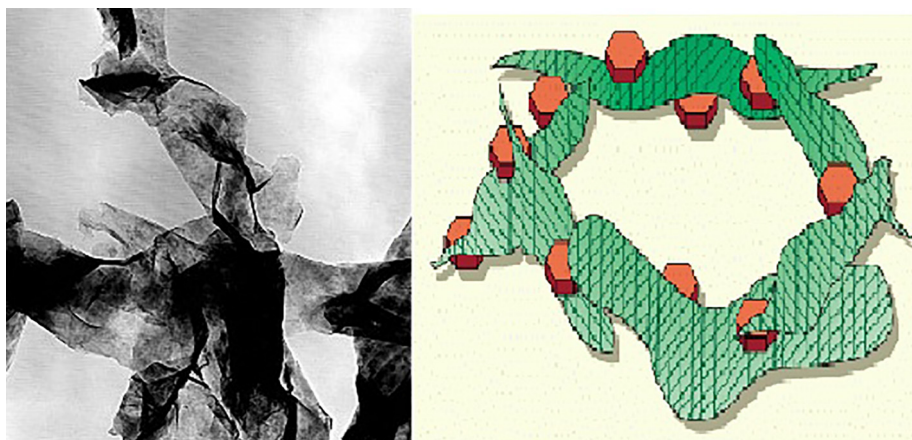


Fig. 3. TEM micrograph and 3D MMH-bentonite gels structure [17].

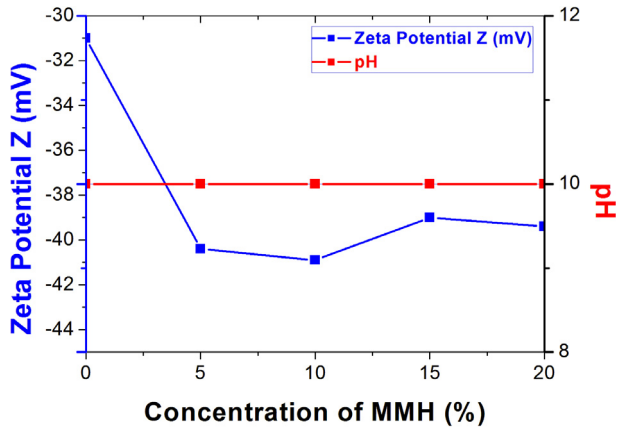


Fig. 4. Zeta potential of Na-Bentonite-MMH suspension.

2. Shear-thinning region in which the viscosity decreases with increasing shear stress as function of shear rate. This result shows that the structural nature of the base suspension (Na-Bentonite 30 kg/m³) is modified by the presence of MMH.

The adsorption of MMH on the Na-Bentonite sheets (with a negative surface charge) significantly increases the viscosity of the Na-Bentonitic suspension.

According to Plank, this increase of viscosity due to a cross linking of Bentonite particles with bridging MMH particles. The oppositely charged Bentonite and MMH particles create a viscous fluid through attraction within a three dimensional (3D) network. The attachment of MMH particles on Bentonite platelets, and also their

common network, can be observed with a transmission electron microscopy (TEM) Fig. 3.

In some cases, even the ideal hexagonal crystal shape of the hydrated MMH particles is visible in Fig. 3. According to EDX-analysis, the particles on the Bentonite platelets exhibit an Mg-Al ratio of about 2.5, and therefore can be identified as MMH [17].

3.2. Zeta potential of suspension Na-Bentonite-MMH

Zeta potential measurement helps to understand the dispersion, aggregation or flocculation phenomena. When the Zeta potential tends to zero, the inter-particle forces decrease. Attractive forces become then preponderant and the particles aggregate. In order to obtain a stable suspension, the objective is therefore to obtain the highest Zeta potential (in absolute value) [19,16].

Zeta potential values in Fig. 4 translates the electric double-layer theorem of Na-Bentonite, an increase in potential with the increase of the concentration of the MMH (–41 mV) to 10% then a remarkable fall after this concentration due to saturation by free cations in suspend and mark a value lower (–37 mV) at 15% and 20% of MMH. The concentration of 10% MMH (Formulation #3 in Table 5) is considered as optimum concentration for Na-Bentonite/MMH suspension which can be used as basic formulation for water-based drilling fluids.

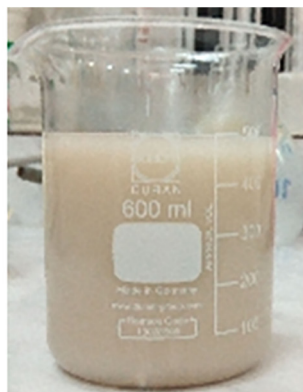
A visual stability of suspensions without adding MMH is illustrated in Fig. 5.

This suspension lost his stability just few minutes after rest and a sedimentation phenomenon is appearing after 15 min; Note that the measured zeta potential is –31 mV.

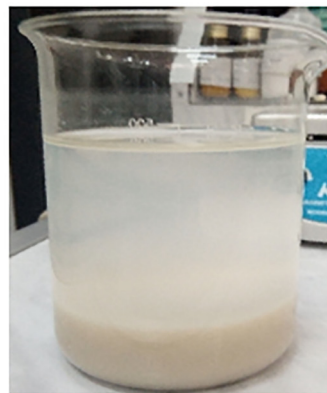
A visual stability of suspensions with 10% MMH illustrate in Fig. 6.

Table 5
Different formulations Na-Bentonite /MMH suspensions.

Components Formulation	Na-Bentonite kg/m ³	Soda ash kg/m ³	MMH % by weight of Bentonite	Water l/m ³	Caustic soda
01	30	0.5	0 (0 kg/m ³)	969.5	Add to Adjust pH = 10
02	30	0.5	5 (1.5 kg/m ³)	968	
03	30	0.5	10 (3 kg/m ³)	966	
04	30	0.5	15 (4.5 kg/m ³)	965	
05	30	0.5	20 (6 kg/m ³)	963	



0 Minutes



15 Minutes

Fig. 5. Stability of Na-Bentonite suspension without adding MMH.

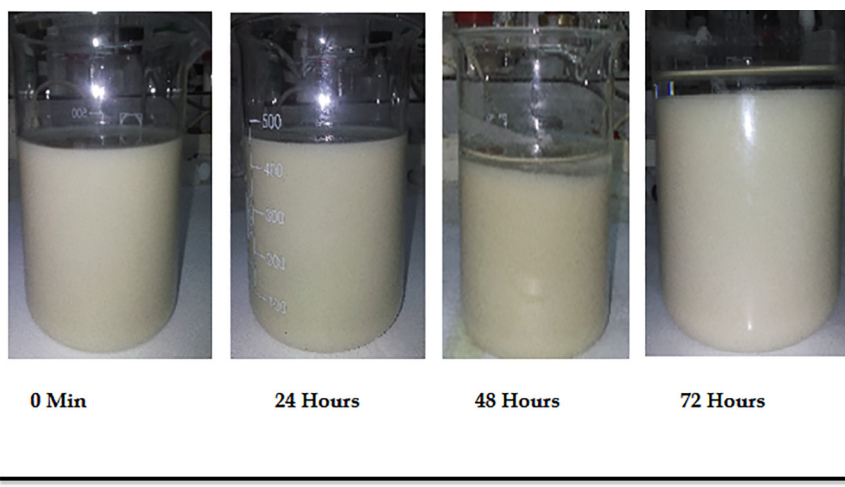


Fig. 6. Stability of Na-Bentonite suspension with 10% MMH.

This suspension has an excellent stability and guards his suspension after 72 h of rest without any settle which gives zeta potential value -41 mV.

4. Conclusion

According to characterization results of Algerian Na-Bentonite, conclude that the current Na-Bentonite is not complies with API 13A and contains impurities in the form of quartz. The improvement of swelling properties of Na-Bentonite is primordial before being used.

The use of mixed metal hydroxide with Algerian Na-Bentonite has proved a lot of advantages in terms of stability and improvement of the suspension characteristics. The addition of MMH increased the yield stress of the Algerian Na-Bentonite suspension significantly with an improvement on the suspension stability (Potential Zeta Measurement), which at 10% of MMH by weight of Bentonite gives the best properties in terms of stability -41 mV with a yield stress of 1.7 Pas.

The relatively weak electrostatic interaction between hydrated MMH particles and Bentonite can be broken easily by shear stress. MMH crystals attach to Bentonite platelets by ionic exchange in which the naturally occurring cations on Bentonite are exchanged with MMH. This forms of association on the face of the clay platelets improves Bentonite hydration and rheological properties of suspension.

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