



DESIGNING OF DRILLING FLUIDS USING NANO SCALE POLYMER ADDITIVES

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Drilling fluids, dispersed systems that have to meet specific technological requirements in order to be used in the process of oil wells drilling have been recently intensely studied. The major aim of the research is to increase the technological efficiency of these systems, to make them environmentally friendly and economical. The paper presents the designing of novel drilling fluids together by applying nanotechnology to wells drilling technology. The author focused on low solid content water-based drilling fluids prepared with polymers. Two polymers were tested to adjust specific properties and their performance was studied comparatively for particles sizes in micro and nano scale. Treatments of alkalisation and density increase were performed on an initial system, evaluating the response to them by measurements on the entire set of standard properties.

INTRODUCTION

Wells drilling is a major part of petroleum industry worldwide and it requires a high level of knowledge and technology.¹ An extremely important role is given to the technology of drilling fluids, which are dispersed systems that must fulfill various functions with direct influence on the drilling operation performance.²

Therefore, in the past decades there has been an increased interest for new products in the area of drilling fluids and extensive researches and developments have been carried out to improve those systems. The main motivation is represented by the technological factor, for instance when drilling at high depths and/or horizontally; another one comes from the strict environmental regulations imposed on toxic and non biodegradable materials, especially in offshore drilling.³

This paper refers to water-based drilling fluids prepared with certain additives that help to adjust one or more properties; these additives are mainly polymers. This wide class of materials is well-known for its industrial applications in different

fields.^{4,5} They are mostly used because of their specific properties such as rheological behaviour,^{6,7} ability to form hydrogels, capacity of interaction with other solid particles by bridging and encapsulation etc.⁸

The use of natural hydrophilic colloids⁹ to the preparation of drilling fluids was introduced first by Chillingarian in 1950.⁹ Among those there was a number of natural gums like: Shiraz, Ghatti and Tragacanth. Since then, polymer additives were introduced and studied to a great extend in oil industry; not only in the drilling technology, but also in reservoir engineering.^{10,11}

The technological advantages of using water based polymer containing drilling fluids are good slurry suspension and transport properties, as the gel process occurs rapidly and the shear stress at low shear rates are high. These qualities also prevent slurry layer formation in the horizontal sections of the slanting hole. In addition, the hydration and dispersion inhibition of the clay that comes from the productive strata, is the result of encapsulating action of the macromolecular chains towards the clay colloids. It can also be mentioned

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the reduction of the friction at the drill pipe because of the slurry encapsulation mechanism and the deposition of a polymeric film on the well walls as well as on the metallic elements of the drill tool. The use of water based polymer containing drilling fluids help to diminish the charge on the solids control equipment at the surface as there is a low solid content.

In the most recent years, nanotechnology has taken a remarkable advance in many scientific fields;^{12,13} the drilling fluids technology, a big profitable domain with a great potential, could not fall apart. Therefore, a particular effort is dedicated to the application of nano technology to the design of drilling fluids, considering the increased flexibility of those systems. Solid nano particles dispersed may offer unique properties to a drilling fluid or can simply influence its properties in certain ways. From a practical point of view, the presence of nano sized solid particles in a drilling fluid is worth to be studied, evaluated and, eventually, controlled. Introducing nano-sized additives in the drilling fluids technology is extremely new and therefore, promising.

EXPERIMENTAL

The preparation of water based drilling fluids involved gradual addition of materials under continuous stirring at 3000 rpm and letting them mix and interact with the system for minimum 30 minutes.

The materials used were: Xanthan gum, a polysaccharide acting as rheology controller, provided by C.P. Kelco; calcium carbonate, weighting agent of fine granulation ($d_{10}<4\ \mu\text{m}$; $d_{50}<25\ \mu\text{m}$; $d_{90}<80\ \mu\text{m}$), commercially named Avacarb, from Ava Drilling Fluids & Services S.p.A.; sodium hydroxide, in aqueous solution 50%, added to adjust the pH, a product of Chimopar S.A. Roumania; a polymer synthesized used as a filtrate reducer additive.¹⁴

The set of standard properties measured for the prepared drilling fluids included: density, determined with the mud

balance; the conventional viscosity using the Marsh funnel; the rheological parameters and gel resistance, calculated with data obtained from measurements at FANN 35A viscosimeter.¹⁵ The rheology study was completed with measurements performed with a Brookfield PVS rheometer. In addition, the filtrate volume was measured with the Baroid filter press; for the filtrate pH the data was acquired using a Techne pHmeter, model 3505; finally, the filter cake thickness was determined with a penetrometer Dreamsience.

The nano particles were obtained by grinding with a Fritsch Pulverisette planetary mill having an agate bowl and 20 agate ball of 20 mm diameter; their particle size distribution was measured by the dynamic light scattering method (DLS) with a Red Badge Nano Sizer Coulter.

RESULTS AND DISCUSSION

The designing of a new water based drilling fluid started taking as a model the Flo-Pro system.¹⁶ The initial mixture was composed by water, Xanthan gum and the fluid loss reducer synthesized by the authors. The additive properties of this polymer are due to its capacity of forming hydrogels by absorption of free water from the system. The material is also pH sensitive, its swelling capacity increases in alkali medium.¹⁷

The optimization of the initial system consisted, first, in a treatment with sodium hydroxide. It resulted in creating an alkali medium of dispersion which increased the efficiency of the viscosifier, the Xanthan gum. Next, a weighting operation with calcium carbonate was done, considering the relative low density that the initial system has.

Table 1 presents the properties of the initial system and of the systems obtained after performing treatments. These properties are density, ρ_n , Marsh funnel viscosity, V_M , apparent viscosity, η_{ap} , behavior index, n , consistency index, k , gel strength at 1 and 10 minutes, θ_1 , θ_{10} , cumulative filtrate volume, V_f , the filtrate pH, and the cake thickness, t .

Table 1

Properties of the initial system and of the systems obtained after treatments

System	ρ_n , kg/m ³	V_M , s	η_{ap} , Ns/m ²	n	k	θ_1 , N/m ²	θ_{10} , N/m ²	V_f , cm ³	pH filtrate	t , mm
A	1000	46	18	0.525	0.48	4.3	5.3	9.0	7.0	0.5
B	1000	49	20,5	0.451	0.92	5.7	6.7	7.3	11.0	0.5
C	1170	48	24	0.494	0.82	5.7	6.7	7.6	9.0	2.3
D	1370	51	33.5	0.483	1.23	5.7	6.7	7.8	8.5	2.8

A – water, Xanthan gum 2.5%wt, fluid loss reducer 3%wt

B – water, Xanthan gum 2.5%wt, fluid loss reducer 3%wt, NaOH

C – water, Xanthan gum 2.5%wt, fluid loss reducer 3%wt, NaOH, calcium carbonate 2.5%wt

D – water, Xanthan gum 2.5%wt, fluid loss reducer 3%wt, NaOH, calcium carbonate 4.5%wt

It can be observed that the pH is 11 after adding sodium hydroxide and has a continuous decrease when adding calcium carbonate. This fact is explained by formation of calcium hydroxide, consuming the OH^- ions existing in the medium after sodium hydroxide dissociation. This treatment has a major impact on the cumulative volume of filtrate by decreasing it, an important improvement to the drilling fluid. Even at lower values of pH, the fluid loss reducer polymer maintains good performances by retaining free water from the system.

When adding the weighting agent, together with adjusting the density, the flow parameters are slightly increased due to the contribution of extra solid particles to viscosity. This effect is explained by the interactions between these chemically inert

particles through static forces, as well as by their interaction with the continuous medium through friction forces. In addition, the presence of calcium carbonate particles may induce a screening effect for the long macromolecular chains and it causes a slight decrease of the behaviour index, k , at the first addition.

As far as the caking phenomena is concerned, the solids laden fluid deposits a thicker filter cake once the calcium carbonate is added. Still, the cake is an elastic and impermeable polymeric film upon which the solid particles settle.

The same set of measurements was performed on a drilling fluid prepared in the same manner, only the polymers were ground to a nano metric scale. After grinding, their particle size was determined, as shown in Fig. 1.

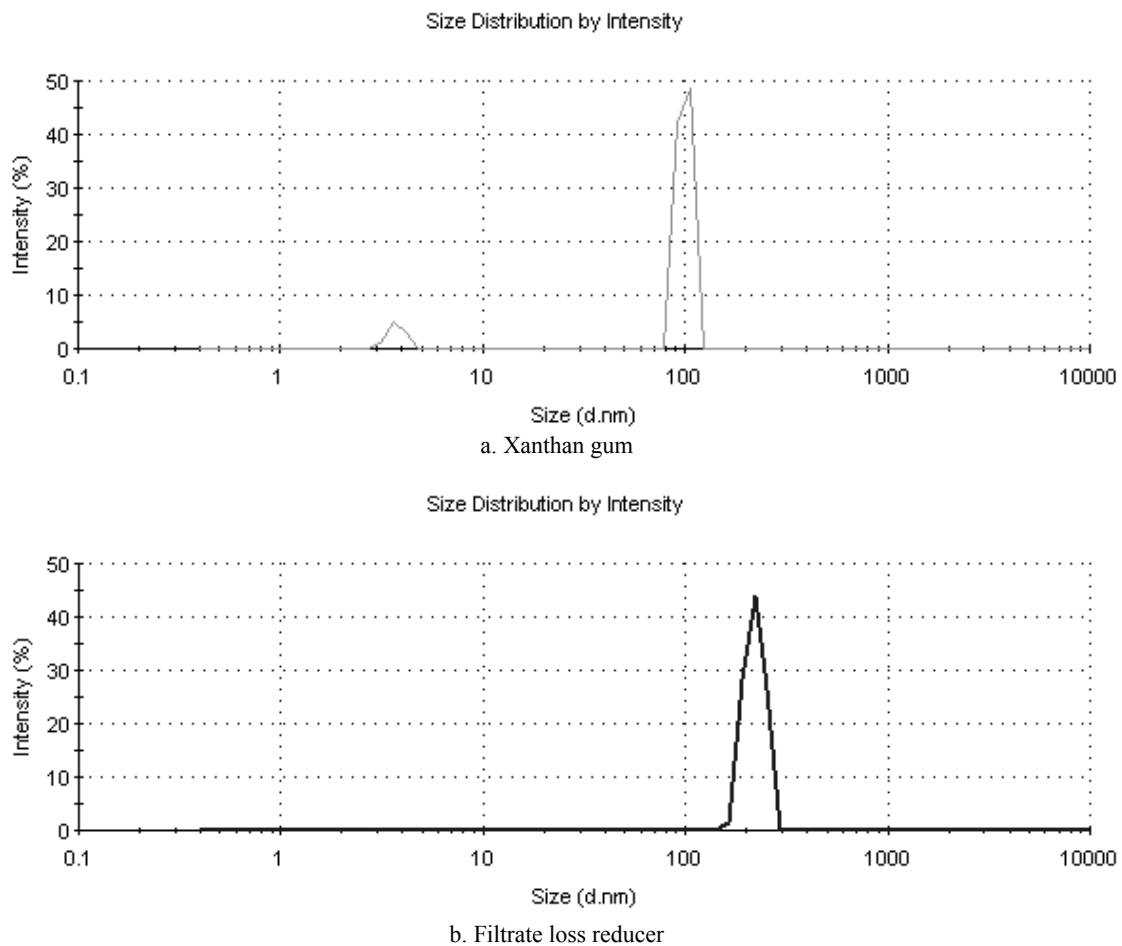


Fig. 1 – The particle size distribution at nanometric scale.

It can be seen that the Xanthan gum has an average size diameter of around 100nm, while the fluid loss reducer was brought to about 200nm. Both particle size curves show an unimodal distribution. Furthermore, when referring to the

nano scale additive, it means these particle size additives.

The values of the measured properties, the same as presented in Table 1, are given in Table 2.

Table 2

Properties of the drilling fluids prepared with nano scale sized additives

System	ρ_n , kg/m ³	V_M , s	η_{ap} , Ns/m ²	n	k	θ_1 , N/m ²	θ_{10} , N/m ²	V_f , cm ³	pH filtrate	t , mm
E	1000	38	14	0.479	0.32	3.2	4.1	6.4	7.0	0.5
F	1000	41	18.5	0.389	0.75	4.3	5.0	3.8	11.5	0.5

E – water, nano Xanthan gum 2.5%wt, nano fluid loss reducer 3%wt

F – water, nano Xanthan gum 2.5%wt, nano fluid loss reducer 3%wt, NaOH

Comparing to the data in Table 1, it is noticeable that the flow parameters are slightly lower for the case of drilling fluids with nano additives, including the gel strength at one and ten minutes rest. Considering that these systems are to be further weighted by adding solid particles, the previous set of measurements showed that the flow characteristics are to be increased. Nevertheless, the influence of pH is obvious in the sense of enhancing the efficiency of the Xanthan gum, the viscosity controlling agent. This aspect is revealed both through the rheological parameters, as well as through the gel resistance.

As far as the fluid loss reducer agent is concerned, it gains better properties of keeping the cumulative volume of filtrate at low values. It is due to the fact that when the polymer is brought to smaller particle sizes, namely to nano metric scale, the total specific area is considerably increased; thus, the interaction area with the continuous

medium is a lot bigger and, so, the swelling capacity of this polymer is more significant. At basic pH, it can be seen that the performance of the fluid loss reducer is clearly intensified, in a synergetic effort with the viscosity controlling agent.

The rheological behaviors of the drilling fluids prepared in this study are presented in Fig. 1. The rheological model considered for the aqueous, free clay and polymer containing systems is the Ostwald de Waele one.¹⁸

A first glance observation of the profiles in Figs. 2 and 3 confirms the choosing of the Ostwald de Waele model. Looking at the graphs in Fig. 2, it is obvious the synergetic effect of pH and of CaCO₃ presence to increase the flow resistance of the system. Meanwhile, as seen from Fig. 3, the flow curves for nanometric scale additives show a similar profile, but at lower absolute values.

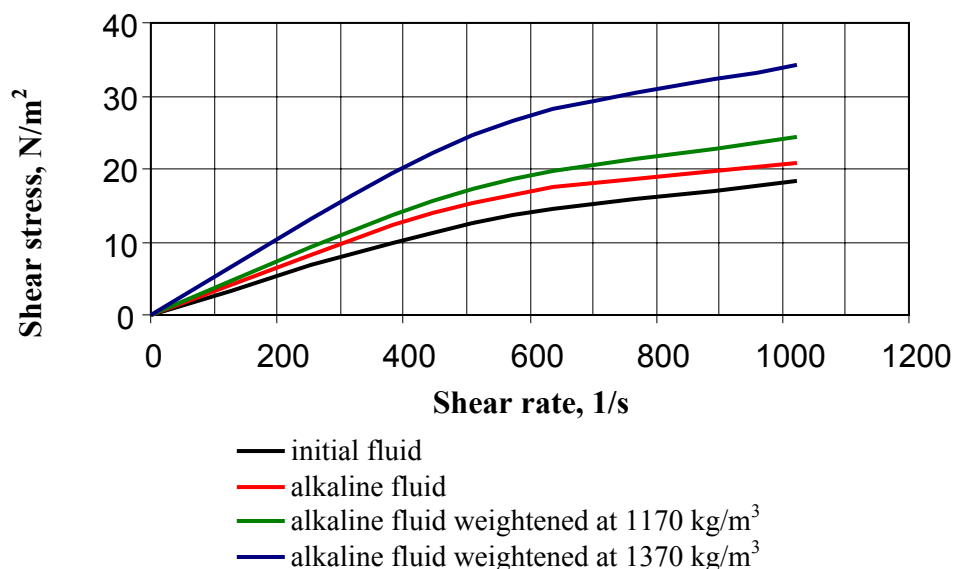


Fig. 2 – Flow curves of the drilling fluids designed with standard sized additives.

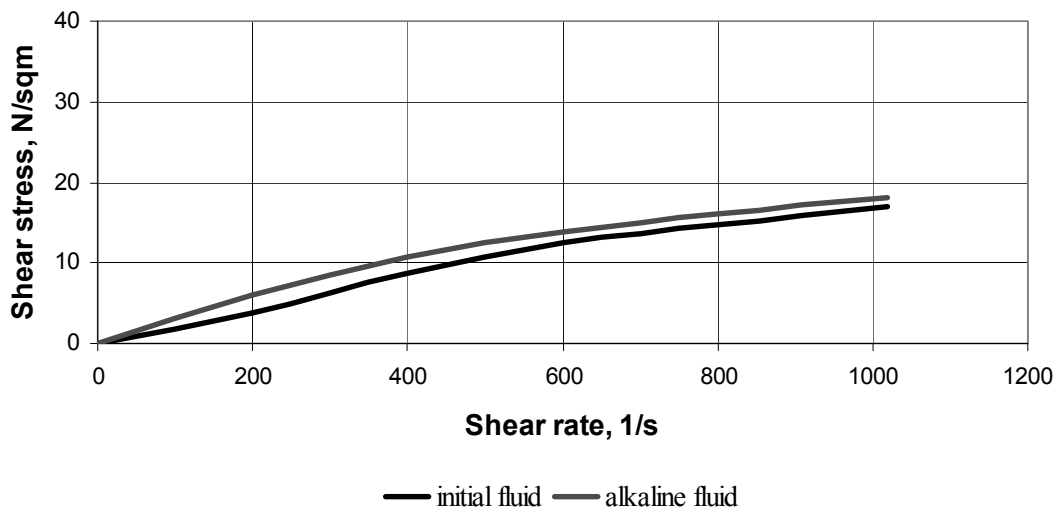


Fig. 3 – Flow curves of the drilling fluids designed with nano metric scale additives.

CONCLUSIONS

This paper is presenting a new approach to the study of drilling fluids by analyzing the influence of additives granulometry to all standard properties. Furthermore, the comparison of drilling fluid performances depending on the particle sizes of the additives used goes to the level of nano scale. It is a breaking through subject in the field of drilling technology.

In addition, the study refers to a new polymer material that is meant to be introduced as fluid loss reducer. Its efficiency and response to different treatments is tested here at laboratory stage.

The experimental results lead to several conclusions. First, the polymer synthesized by the authors provides good fluid loss reduction, both in neutral medium and, especially, in alkali medium. In addition, the fluid loss reducer is more efficient if ground to nanometric sizes.

In an alkali medium, after adding sodium hydroxide, the efficiency of the Xanthan gum, as a viscosifier, is better; the weighing treatment with calcium carbonate has a flocculating effect, seen by the increase of the filtrate volume and higher rheological parameters.

The materials used to formulate the drilling fluids in this study act in synergy to create dispersion with good structure properties, though at nano metric scale, the additives are not more efficient; the gel strength increases when adding a small amount of calcium carbonate, then remains constant when increasing the amount of it.

The drilling fluids designed in this study are viable and robust systems, compatible to other systems, already existing on the market.

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REFERENCES

1. J. Bergenholtz, J. F. Brady and M. Vicic, *J. Fluid Mech.*, **2002**, 456, 239.
2. R.P. Chhabra and J.F. Richardson, “Non-Newtonian Flow and Applied Rheology”, Second Edition: Engineering Applications, Butterworth-Heinemann/ICHEME, 2008.
3. ASME Shale Shaker Committee, “Drilling Fluids Processing Handbook”, Elsevier, 2005.
4. K.W. Lem, J.R. Haw, D.S. Lee, C. Brumlik, S. Sund, S. Curran, P. Smith, S. Brauer and D. Schmidt, *Nanotech.*, **2010**, 1, 889.
5. M. Manea, *Rev. Chim. (Bucharest)*, **2009**, 60, 1231.
6. G.V. Chilingarian and P. Vorabutr, *Dev. Petr. Sci.*, **1981**, 11, 17.
7. A. Y. Dandekar, “Petroleum Reservoir Rock and Fluid Properties”, CRC Press, 2006.
8. W.B. Russel, D.A. Saville and W.R. Schowalter, “Colloidal Dispersions”, Cambridge University Press, 1999.
9. Y. J. Azar and G. R. Samuel, “Drilling Engineering”, PennWell Co., SUA, 2007.
10. C.J. Tucker, *Nanotech.*, **2010**, 1, 846.
11. M.G. Popescu and M. Manea, “Fluide de foraj și cimenturi de sondă. Îndrumar de laborator”, UPG Ploiești, 2008.
12. M.G. Popescu, “Fluide de foraj și cimenturi de sondă”, UPG Ploiești, 2002.
13. C.S. Satish, K.P. Satish and H.G. Shivakumar, *Indian J. of Pharm. Sci.*, **2006**, 68, 133.

14. M. Manea, C.G. Dussap, J. Troquet and L. Avram, *Le 4^{ème} Coll. Fr.-Rou. de Chim. Appl. (Clermont-Ferrand)*, **2006**, 171.
15. D. Urban and K. Takamura, "Polymer Dispersions and Their Industrial Applications", Wiley-VCH, 2002.
16. P.A. Williams, "Handbook of Industrial Water Soluble Polymers", Wiley-Blackwell, 2007.
17. R.K. Gupta, "Polymer and Composite Rheology", Marcel Dekker, 2000.
18. G. Allan Stahl, D.N. Schulz, "Water-soluble Polymers for Petroleum Recovery", Springer, 1988.