STUDY OF THE NANOPARTICLE / POLYMER / $CACO_3$ INTERACTIONS TO OPTIMIZE THE STABILITY OF THE COLLOIDAL SUSPENSION AND THE PACKING OF THE SOLIDS

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Abstract

Nowadays, interest in nanotechnology in drilling and completion operations has increased to reduce the formation damage and improve the properties of the drilling fluids. In this way, this study aims to evaluate the effect of the SiO_2 nanoparticles in a drill-in fluid (polymer and calcium carbonate) to minimize its impact in the formation damage based on the filtration and thickness mudcake reduction through the interaction polymer/nanoparticle/calcium carbonate. Rheological behavior of the polymeric solution and the drilling fluid in absence and presence of nanoparticles were evaluated. Additionally, the static and dynamic filtration test was carried out under reservoir conditions. SiO_2 nanoparticles exhibited an increase in the viscosity of the polymeric solution and drilling fluid due to and polymer adsorption onto nanoparticles surface. Drilling fluid with the addition of SiA nanoparticles reduced and stopped the filtration volume by 77%, decreasing the formation damage by 51% and hence increased the permeability returns by 74% compared to the drilling fluid without nanoparticles.

Keywords: formation damage; drilling fluids; nanoparticles

Resumen

Recientemente, el interés en la apliación de la nanotecnología en las operaciones de perforación y completamiento de pozos ha aumentado con el objetivo de reducir el daño de la formación y mejorar las propiedades de los fluidos de perforación. En este sentido, el objetivo de esta investigación es evaluar el efecto de las nanopartículas de SiO_2 en un fluido de perforación limpio *(polímero y carbonato de calcio) para minimizar su impacto en el daño de formación en función de la reducción del volumen de filtrado y espesor del revoque a partir de las interacciones polímero/nanopartícula/carbonato de calcio. Se evaluó el comportamiento reológico de la solución polimérica y del fluido de perforación en ausencia y presencia de nanopartículas. Adicionalmente, se llevaron a cabo pruebas de filtración estática y dinámica en condiciones de yacimiento. Las nanopartículas de* SiO_2 *mostraron un aumento en la viscosidad de la solución polimérica y del fluido de perforación debido a la adsorción del polímero en la superficie de las nanopartículas. Finalmente, el fluido de perforación con la adición de las nanopartículas SiA redujó y detuvó el volumen de filtración en un 77%, disminuyendo el daño de formación en un 51% y, por lo tanto, aumentó la recuperación de la permeabilidad en un 74% en comparación con el fluido de perforación sin nanopartículas.*

***Palabras claves**: daño de formación; fluidos de perforación; nanopartículas*

1. Introduction

One of the strategies in the design of water-based drilling fluids is the build-up of a low-thickness and permeability filter cake. The particle size of the bridging material has been optimized, polymers have been used as filtration control and viscosifying additives, and other additives such as dispersants to favor the filter cake formation. However, the importance of the colloidal phenomenon in the drilling fluid has been overestimated. In drilling fluid, different compounds are dispersed to have a stable suspension. However, when the particles are not small enough, the fluid is contaminated, the pH is altered, among others; the suspension does not exhibit the necessary stability. That is, particles can begin to flocculate and decant rapidly due to the increased attraction of Van der Waals forces between particles. Once the aggregates are placed on the face of the well, a plaster is obtained with high roughness, thickness, permeability, and porosity that allows the filtering flow through.

Recently, nanotechnology has been used in the drilling and completion operations to inhibit the formation damage and increase the wellbore stability reducing the filtration volume and building an efficient filter cake. Moreover, the use of polymers and the adequate sizing of calcium carbonate ($CaCO_3$) additionally reduce the formation damage rather than the bentonite water-based muds (BWBM) (Suri and Sharma 2004).

Although drill-in fluids (polymer and $CaCO_3$) have better performance in the inhibition of formation damage, there are few studies (Contreras et al. 2014, Srivatsa and Ziaja 2012) of the application and systematic evaluation of nanoparticles in these fluids to improve the properties of the mudcake and reduce the filtration volume. Only Srivatsa and Ziaja (2012) evaluated 0.1 wt% of SiO_2 NPs as a substitute for calcium carbonate in a BFWBM. The authors carried out a series of LPLT and HPHT filtration test, obtaining a reduction in mud filtrate of 50%. In this study, the authors did not report the dynamic evaluation type coreflooding at reservoir conditions.

Additionally, in the specialized literature, there are no studies that evaluate the interaction between polymer/nanoparticle/$CaCO_3$ in the reduction of filtrate loss and the mudcake thickness in a drill-in fluid under dynamic and static conditions of high pressure and high temperature, as well as the estimation of formation damage under reservoir conditions based on the coreflooding test. Therefore, this study aims to evaluate the effect of the SiO2 nanoparticles in a drill-in fluid (polymer and calcium carbonate) to minimize its impact in the formation damage based on the filtration and thickness mudcake reduction through the interaction polymer/nanoparticle/calcium carbonate).

2. Methodology

Materials. The drill-in fluid used presents a typical formulation of a mud widely implemented in the drilling of Colombian wells: deionized water, caustic soda (NaOH) to adjusted pH, xanthan gum, and calcium carbonate. Ethanol, ammonium hydroxide, tetraethyl orthosilicate (TEOS) were used to synthesize the SiO_2 Nps. For the surface modification of the nanoparticles was used hydrochloric acid.

Synthesis and characterization of silica nanoparticles. Silica nanoparticles were synthesized through Sol-Gel Method using TEOS as silica precursor, ethanol as co-solvent, ammonia as a catalyst and deionized water based on the Stöber method (Stöber, Fink, and Bohn 1968). The surface modification was carried out, adding 0.5 g of Nps to an aqueous solution to a pH of 3 adding HCl (Betancur et al. 2016). The nomenclature of nanoparticles was done as follow: SiA for the nanoparticle-treated with an acid solution and SiC to the fumed nanoparticle. Finally, nanoparticles were characterized by the determination of the hydrodynamic diameter and zeta potential using dynamic light scattering (DLS). Functional groups of the nanoparticle surface were identified through Fourier transform infrared spectroscopy (FTIR).

Polymers preparation and characterization. The XG polymer solution was prepared according to the concentration employed in the formulation of the drilling fluid (XG polymer and water solution), see table 1. Rheological measurements of the polymer solutions in the presence and absence of SiO_2 nanoparticles were performed using a rotational rheometer. Tests were conducted at 77°C in a shear rate range of 1 to 100 s^{-1}. The adsorption tests were performed in batch–mode experiments by fixing the amount of SiO_2 nanoparticles equivalent to employed in this study 0.1 wt% (1000 mg. L^{-1}) and varying the concentration of polymer (100 to 2500 mg. L^{-1}) according to the procedure described by (Guzmán et al. 2016) at 25°C.

Drilling fluids preparation and characterization. The drilling fluid was prepared by mixing each additive and concentration indicated in table 1 in the mixer. Drilling fluids were characterized by the determination of the basic properties: density, pH, and solid content according to the standard protocol of the American Petroleum Institute (API 2003). Rheological properties of the drill-in fluid were measured using a rotational viscometer Fann to determine the rheological parameters: plastic viscosity (PV) subtracting the Fann values at 600 and 300 rpm, θ_{600} and θ_{300}, yield point (YP) subtracting the PV and the Fann value at 300 rpm, and gel strength (GS) at 10 seconds and 10 minutes (Gel 10s / 10m) reading the maximum dial at 3 rpm after at the respective time. HPHT filter press of 175 ml was used to register the filtration volume a static condition of pressure and temperature, 500 psi and 104°C. The thickness cake was measured at the end of the test.

Addtive	Concentration (g)
Deionized water	340
Xanthan gum	0.5
SiO_2 nanoparticles	0.1%
Calcium carbonate	23

Table 1— Laboratory formula to prepare the equivalent of 1 barrel (1 bbl) of drill-in.

Displacement tests. Nanoparticles with the highest filtration performance were evaluated under temperature, overburden, pore, and overbalance pressure conditions: 87°C, 3000 psi, 1200 psi, and 1700 psi, respectively. Two cores (porosity 13%), crude oil (11° API - viscosity of 6000 cP at 25°C), and brine from the Colombian Castilla field were used. The experimental protocol consisted of:

- The effective oil permeability (Ko) was evaluated by injecting crude oil
- For the evaluation of the dynamic filtration behavior, the cores were saturated again with crude oil. Then, the circulation of drilling fluid was carried out in the core face, and the filtration volume was measured each minute.
- Finally, crude oil was injected until the pressure drop stabilized to evaluate the Ko return.

3. Results

Nanoparticles characterization. The hydrodynamic diameter (dp_{50}), the isoelectric point, and the zeta potential of the different SiO_2 nanoparticles are presented in Table 2. SiA and SiC nanoparticles presented a dp_{50} of 11.3 nm and 7.0 nm, respectively. Zeta potential of the SiA y SiC nanoparticles at pH of work showed -45.55 and -39.47, respectively, values more negative than -30 mV, indicating good stability and dispersion inside the drilling fluid (Mahmoud et al. 2016).

Nanoparticles	dp_{50} (nm)	Isoelectric point	Zeta potential (mV) @ pH 10 and 50°C
SiA	11.2 ±	1.9	-45.55 ± 3.41
SiC	7.0 ±	2.6	-39.47 ± 5.64

Table 1— Mean hydrodynamic diameters (dp_{50}), isoelectric point, and zeta potential to pH work of the synthesized and fumed SiO_2 nanoparticles

Fig. 1 shows the FTIR of SiA and SiC nanoparticles. SiO_2 nanoparticles evidence the same bands with a change in the intensity of transmittance in the bands centered at 3400, 1635, 1215, and 806 cm^{-1}. The prominent band between 3600 to 3000 cm^{-1} can be related to the vibrations of the stretching and bending of the free -OH groups on the nanoparticles surface (Panwar, Jassal, and Agrawal 2015). Moreover, the band at 1635 cm^{-1} could correspond to molecules of water adsorbed in the surface of the nanoparticle, while the band between 1000 and 1300 cm^{-1} related to the Si-OH stretching and Si-O-Si symmetric stretching. Furthermore, siloxane (O-Si-O) symmetric vibrations appear at about 806 cm^{-1} (Beganskienė et al. 2004, Montes, Cortés, and Franco 2018). The difference spectrum between SiA and SiC materials can be attributed to the greater presence of -OH groups on the surface of the nanoparticles due to the synthesis.

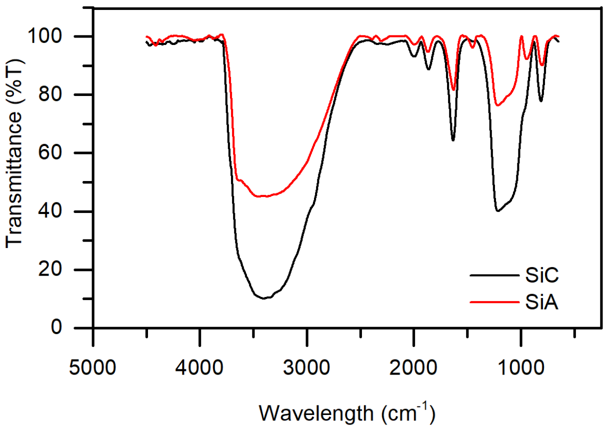

Fig. 1— FTIR spectrum of the fumed silica (SiC) and synthesized acidic surface modification silica (SiA) nanoparticles.

Polymer characterization. Fig. 2 shows the adsorption isotherms when the SiA and SiC nanoparticles dosage was fixed in solutions with a different concentration of XG polymer. Isotherms obtained corresponded to the Type I, according to IUPAC (Thommes et al. 2015). Hence, the concentration of polymer rises, the aggregate size increase (see Fig. 3), the attractive forces became stronger, and there was and auto-associative activity due to the functional groups of the polymer, resulting in a reduction of the capacity of the interactions with the nanoparticles and hence in the amount absorbed. Rapidly, the systems adsorbed reach the saturation of the available surface area, so the graph resulted in a plateau for high concentrations of the polymer. The SLE model described in a right way the experimental results with values of RMS% < 10%, see table 2. Additionally, it can be observed that the H and K parameter for the SiC nanoparticles corresponded to the lowest and highest value, respectively, compared with the SiA nanoparticles. This could be that the surface of SiC nanoparticles had a great affinity and rapid association with the polymer molecules. Additionally, the $N_{ads,m}$ of the isotherm corresponding to SiC nanoparticle is greater than Si11A; this adsorption capacity could increase or conserve the rheological properties of the polymer adsorbed. The adsorption that occurs in the polymer – SiO_2 nanoparticle system nanoparticles occurs mainly due to silanol functional groups on the nanomaterial surface, -OH groups, and the free radicals in the polymer chain of XG and the carboxylic groups -COOH (Kennedy, Kent, and Brown 2015). According to the FTIR spectrum of the SiC nanoparticles, this material presented a greater presence of -OH groups on the surface, this could explain why affinity is more pronounced for the SiC nanoparticles and XG polymer interaction.

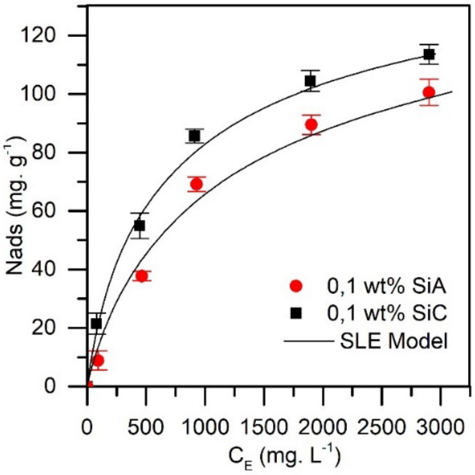

Fig. 2 — Adsorption and desorption isotherms of XG polymer onto SiA and SiC nanoparticles (1000 mg. L-1) obtained varying the initial polymer concentration (100-2500 mg. L-1) and a fixed temperature of 25°C.

Nanoparticles	$H\,(mg.g^{-1})$	$K\,x\,10^{-3}(g.g^{-1})$	$N_{ads,m}(mg.g^{-1})$	RMS%
0.1 SiA	5.13	6.8	189.24	10.16
0.1 SiC	2.91	9.8	195.32	9.23

Table 2 — Estimated parameters of SLE model for adsorption of polymer onto SiA and SiC nanoparticles obtained varying the initial polymer concentration and a fixed temperature of 25°C.

The rheology of the polymer solution in the absence and presence of nanoparticles is shown in Fig. 3 together with the Herschell-Buckley (HB) model fitting. The viscosity of the polymer solutions decreased as the shear rates increased with a typical behavior of pseudoplastic fluid or shear-thinning fluid. At low shear rates, the stretching polysaccharide molecules intertwine to form aggregates that cause high viscosity. As the shear rate is increased, the aggregates are destroyed, the molecules orient along the flow direction, and the apparent viscosity decreases (Hamed and Belhadri 2009, Han 1976). The viscosity of the polymer solutions increased with the presence of 0.1 wt% of SiO_2 nanoparticles and was explained through the interaction of polymer molecules with silanol and siloxane groups of nanoparticles via hydrogen bonding (Giraldo et al. 2017, Kennedy, Kent, and Brown 2015). However, the effect in the polymer sample with SiC nanoparticle is higher; the average increase at the entire shear rate evaluated was up to 15.4%.

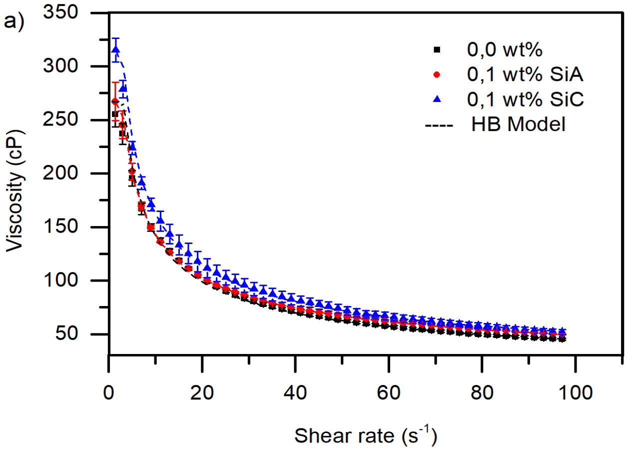

Fig. 3 — Viscosity as a function of the shear rate for the polymeric solutions in the absence and presence of 0.01 wt% SiA and SiC nanoparticles at 77°C during 16 h.

Drilling fluid characterization. Density, pH, and the solids content were in the absence and presence of 0.1 wt% SiA and SiC nanoparticles. Density was not altered for the addition of any silica nanoparticles with values of 8.9 ± 0.1 lb/gal. Additionally, the addition of the nanoparticles did not alter the pH values. Finally, the solids content was 2.0 ± 0.1wt% for all samples and can be classified as low-solid drilling fluids according to Caenn, Darley, and Gray (2017).

Table 2 shows the rheological properties PV, YP, and GS for the drill-in fluid in the absence and presence of 0.1 wt% of SiA and SiC nanoparticles. It can be seen that PV was increased by 11 and 13% due to the addition of 0.1 wt% SiA and SiC nanoparticles, respectively. Moreover, the YP values for the fresh samples increased by 15% for the SiC nanoparticles, and any change for the SiA nanoparticle. Finally, GS increased by 25 and 20%, respectively for the addition of 0.1 wt% SiA nanoparticles; whereas SiC nanoparticles increased by 50 and 40% for the same period. At ultra-low velocity, the drilling fluid has its highest yield stress values and in static condition will develop gel structure that aid in the particle solids suspension, this behavior more remarkable for the SiC nanoparticles.

Nanoparticles (wt%)	VP (cP)	YP (lb/100 ft^2)	GS (lb/100 ft^2)
0	36	25	4/5
0.1 SiA	40	25	5/6
0.1 SiC	41	29	6/7

Table 2 — Rheological properties PV, YP, GS for the drill-in fluid in the absence and presence of 0.1 wt% of SiA and SiC nanoparticles

Table 3 shows the filtrate volume and mudcake thickness in the HPHT filtration test of the drill-in fluid in the presence and absence of 0.1 wt% SiA and SiC nanoparticles, at 500 psi and 77°C. The SiA and SiC nanoparticles exhibited the same behavior of reduction of the filtration volume and thickness mudcake up to +11 and 66% compared with the drilling fluid in the absence of nanoparticles. It is evident the enhanced of the mudcake properties. First, SiO_2 occupied the space between the micrometric material and increased the drilling fluid viscosity reducing the filtration volume. Additionally, adsorption isotherm presented and interaction between XG polymer – nanoparticles that verified the results above. Also, SiC nanoparticles presented the highest adsorption capacity; in this way is probably that this nanoparticle enhances rheological properties of the drilling fluid and subsequently reduce the filtration volume and thickness mudcake.

	0.0 wt%	0.1 wt% SiA	0.1 wt% SiC
Filtration volume (mL)	18.0	15.0	15.6
Mudcake thickness (mm)	0,200	0,060	0,061

Table 3 — Rheological properties PV, YP, GS for the drill-in fluid in the absence and presence of 0.1 wt% of SiA and SiC nanoparticles.

The Ko without damage was 1232 ± 5 mD. After exposure to the drilling fluid in the absence of nanoparticles, the Ko was reduced to 402 ± 5 mD, that corresponds to a 67% of damage due to an increase of the viscosity of the oil effluent. The Ko return was 169 ± 1 mD, increasing the damage by 18%. However, in a scenario with nanoparticles, the Ko decreased until to 1030 ± 8 mD, representing a reduction of the formation damage of 76% and can be attributed to the reduction of mud filtrate and the effective formation of the mudcake.

Filtration curves during exposure of the Drilling fluid in the absence and presence of 0.1 wt% SiO_2 nanoparticles are presented in Fig. 4. The drilling fluid without nanoparticles filtrated 43 mL of to the core during an exposure time of 576 minutes. During the first 50 minutes, the 50% of the total filtrate volume entered until the formation of the cake, which was still not impermeable and allowed the filtration even after 500 minutes. In the presence of the SiO_2 nanoparticles, the filtration volume was 9.8 mL for 80 minutes. In this case, the mudcake was formed quickly, and it was impermeable in the first minutes of exposure. The presence of the nanoparticles leads to a reduction of 77% in the drilling fluid filtrate regarding the system in the absence of nanoparticles. Also, the filtration time was reduced by 87%. Corroborating that nanoparticles deposit in the mudcake, fill the empty spaces between calcium carbonate particles, and reduce the permeability and the porosity of the cake.

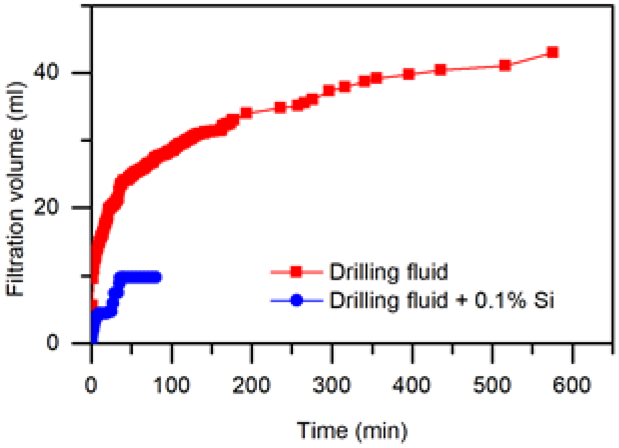

Fig. 4 – Filtration volume as a function of the time during the dynamic filtration displacement test in a sandstone core during the circulation over the coreface of the BFWBM in presence and absence of 0.1 wt% Si11A Nps.

4. Conclusions

HPHT filtration test was carried out for silica nanoparticles of different size, acid surface, and consequently zeta potential. The nanoparticles presented a reduction of the filtration volume and thickness mudcake.

The adsorption isotherms of XG onto SiO_2 nanoparticles were successfully obtained through batch-mode adsorption experiments. Adsorption isotherms showed a Type I behavior. Additionally, the SiC nanoparticles were the most affinity with the polymer.

All the rheological studies between XG-SiO_2 nanoparticles system presented a shear thinning behavior with low yield stress; it was shown that the Herschel–Bulkley rheological model described all samples. The viscosity of the fresh polymer solutions increased with the presence of 0.1 wt% of nanoparticles and was explained through the interaction of polymer molecules with silanol and siloxane groups of nanoparticles via hydrogen bonding.

Nanoparticles added in the drilling fluid reduces the filtration volume in a factor of 77%, and they reduce the effective permeability to oil 16% compared with the base mud that generates a reduction of 67% under the conditions of dynamic filtration reported in this study. Finally, upon the addition of nanoparticles to the drilling fluid, the viscosity of the crude oil was reduced until 9 pore volume injected (VPI), the maximum reduction was of 28% at the maximum shear rate.

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