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## Article

# Advances in functionalized Nanoparticles based drilling inhibitors for oil production

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## Review article

## Advances in functionalized Nanoparticles based drilling inhibitors for oil production

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## ABSTRACT

Oil and gas have been facing various difficulties in well drilling due to shale hydration and swelling when in physical contact with water. Oil-based muds (OBMs) and synthetic based muds (SBMs) have been shown to have superb effort to address the drilling problems of wellbore instability due to the shale hydration. Nevertheless, OBMs and SBMs compositions are threatened agent to the environment which makes water-based muds (WBMs) as viable alternatives. WBMs usually require shale inhibitors, otherwise, water in the fluid may diffuse into the shale formation to cause a fracture, swelling/hydration and delamination of shale. Conventional inhibitor such as KCl is known for its good shale activity but not ecofriendly. Other compounds including amines, imines, and their polymers; gelatin, ionic liquids, the natural compound as well as graphene and graphene composites that have been tested by various authors either have HTHP or the environmental limitation or fail in their application in plugging pore throats in shale. Nanomaterials with a wide range of nanosizes have been detected to greatly hinder shale swelling due to their ability to plug micro-openings in shale by forming compact filter cake to minimize fluid loss and prevent downhole pressure transmission. This review paper is structured to give an overview of shale inhibitors, show the defaults in the convention inhibitor and the viability of nanoparticles as efficient, cheap and sustainable inhibitors.

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## 1. Introduction

Drilling fluid is generally used in oil and gas wells and even in water boreholes drillings. Series kind of fluids is being employed in drilling such that specific fluids are used at the different zone of the wellbore or combination of fluids to facilitate the operation. Drilling fluid is widely categorized into gas

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and liquid. Gaseous fluids include air, air/water (aerosol) and air/polymer (foam) while liquid drilling fluids (drilling muds) comprises of water-based mud (WBM), oil-based mud (OBM) and the synthetic-based mud (SBM) also called low toxicity oil-based mud, LTOBM) (Bol et al., 1994).

The major roles of drilling fluid are to provide hydrostatic pressure to protect invasion of wellbore by formation fluids; sealing of porous formation, its pressure control and prevent damage of the formation; cleaning, cooling and lubrication of bit while drilling and other component; suspension and mobility of drilling cuttings from subsurface to surface; ensure well stability; allow assessment of formation among other (Zakaria et al., 2012). In order to suit these purposes, numerous chemical additives are introduced into the fluid in formulation ratio for suitable rheological properties coupled with their compatibility.

## 2. Well drilling challenges

Shales are generally defined as low-permeable phyllosilicate sedimentary rocks consisting of different clays with other minerals. Their permeability and porosity capacity depends on the proportion of clays and the minerals to one another. Thus, the formation could range from highly hydrated gumbo to a very hard brittle shale (Bol et al., 1994; Hansen et al., 2012).

The sequence of difficulties are usually encountered during oil and gas as well as water wells drilling operations. These include wellbore instability (sloughing formations which could cause tight hole conditions, bridges, torque and drag, and fillings), shale swelling or hydration, formation damage, low rate of penetration, string corrosion and stickiness, the elevated temperature at the bit among others. For instance, if the hole is big, it becomes weak and difficult to stabilize, resulting in problems such as low annular velocities, poor hole cleaning, solids loading and poor formation evaluation (logging). (Rahman et al., 2000; Lyu et al., 2015; Yuxiu et al., 2016)

About 70% of wellbore instability problems are associated with shale (An and Yu, 2017). Shale instability is initiated by the existence of clay minerals such as kaolinite, smectite, and montmorillonite as a result of their great affinity with the water (Aftab et al., 2017). Nevertheless, clay mineral starts swelling after it interacts with the water and raising the wellbore instability like shale sloughing, tight hole, caving and reducing the efficacy of mud to lift the drilled cuttings. (Rana et al., 2019) The clay swelling also decreases the rate of penetration because of the bit balling with a sticky clay.

The mechanism of shale–water interaction may either be physical, mechanical or chemical. The physical and mechanical means involve pore pressure due to osmotic pressure generated by differences in chemical potential during drilling. This results into pressure transmission from the drilling fluid hydraulic pressure to the shale causing instability (Van Oort, 2003). Hence, the downhole (downstream) pressure decreases as the time goes on as a result of chemical potential changes (Tan et al., 1996). The water transport into shale may generally be in the form of osmotic (diffusion) or reverse osmosis (hydraulic pressure difference) or both. The chemical types of water movement into shale formation include chemical interactions, dispersion, and ion-exchange or adsorption (Zhang et al., 2015).

Since shale is made up of octahedral clay sheets of aluminum central atoms or sometime with other metallic atoms like magnesium, calcium etc. sandwiched between two tetrahedral sheets with silicon center, it reacts with water molecule and its other ionic composition due to aluminum affinity for water and chemical potential difference respectively. This led to weakening of electrostatic or van der Waal's forces between the clay silicate layer and dispersion (El-Swaify and Emerson, 1975; Berthonneau

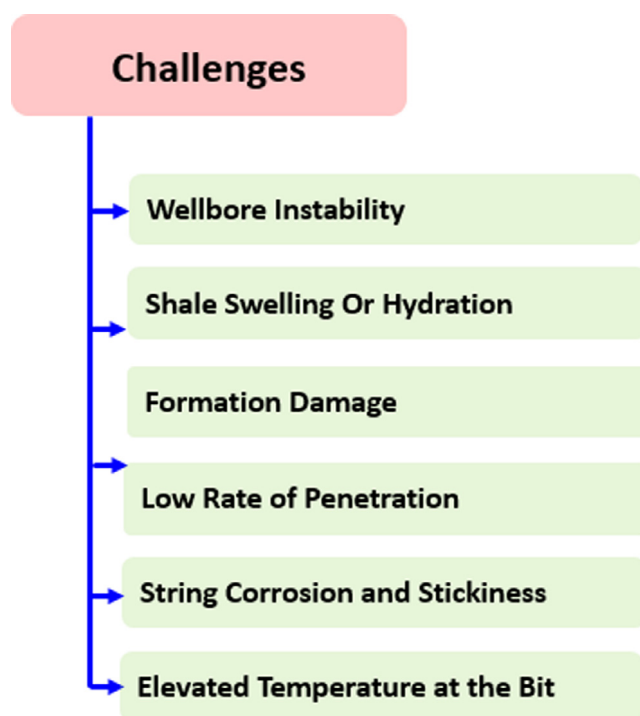


Fig. 1. Difficulties encountered during oil and gas as well as water wells drilling operations.

et al., 2017). Pressure difference between the shale pore and the drilling fluid as well as the chemical potential between the pore liquid and mud fluid possess significant forces that causes unstable wellbore (Lomba et al., 2000). For instance in a brittle shale, formations fracture could be distorted and penetrated the network of the fractures by overbalance mud. This could lubricate surface of the fractures and consequently leads to wellbore and pore pressure equilibration, and finally shale failure (Zhang et al., 2015). In shales, mud weight is usually sufficient to balance formation stress, as these wells are usually stable. With water-based mud, chemical differences could cause interactions between mud and shale that lead to softening of rock. Highly fractured, dry, brittle shales could be extremely unstable leading to mechanical problems (Bol et al., 1994; Yuxiu et al., 2016) (see Fig. 1).

## 3. Types of drilling muds

Drilling muds are used to control hydrostatic pressure in the drilling operation, to transport cuttings from subsurface through the annulus to surface and to cool and clean the bit in the hard geological layer during long time drill. However, all these could be attained through excellent rheology (Mao et al., 2015). The three types of drilling muds that are used in drilling industries are WBM, OBM and SBM (Bol et al., 1994; Lyons Williams, 1996).

WBM majorly contains bentonite and other chemicals additive such as barite (as weight material), thickener (such as xanthan gum, glycol, polyanionic cellulose (PAC), starch, guar gum), calcium carbonate, caustic soda, soda ash, and shale inhibitor. Almost 80% of the mud is made up of water while the rest 20% are additives. About 80% of wells drilling in the oil and gas industries are achieved using WBM due to its environmental friendliness, easy geotechnical analysis and less cost (Aftab et al., 2017). However, WBM is susceptible to a large amount of shale hydration because of great interaction between water in the mud and shale formation composition of the drilling well as a result of chemical differences, hence, leading to wellbore instability.

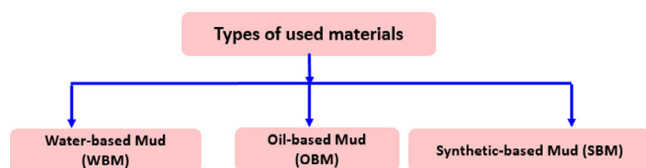


Fig. 2. Commonly used types of drilling muds in drilling industries.

On the other hand, oil-based mud (OBM) and synthetic-based mud (SBM) have excellent shale inhibition, easy cleaning and lubricity properties, although relatively expensive compared to WBM. OBM contains oil continuous phase and dispersive water phase in combination with wetting and gelling agents and emulsifiers. The oil component may be diesel, fuel oil, kerosene and other forms of crude or mineral oils while the water part may be freshwater or sodium or calcium chloride solution. Lyons Williams (1996) OBM and SBM reduced the shale swelling due to less water in the composition which makes them suitable for drilling in highly water-sensitive shales zone. In addition, they could withstand high-temperature deep drill that usually leads to dehydration of WBM and prevents stickiness and balling of the bit. Conversely, their utilization in wells drilling is limited due to their environmental toxicity capacity of when used and cuttings disposal, high cost, poor formation logging during drilling and sometimes constitute damage of formation (An et al., 2015a,b).

WBDFs are and are environmentally friendly (Yang et al., 2017). Water-based drilling fluids performance outweighs that of the oil and synthetic mud systems which makes them be widely used in oil-well drillings. They are preferred because of their excellent ECD management, environment friendliness, better rate of penetration, low cost and toxicity and have no influence on well logging, (An et al., 2015a,b; Guancheng et al., 2016; Yang et al., 2017). However, their use is associated with instability challenges such as cuttings degradation, fluid loss, bit balling, stuck pipe and so on resulting from shale interaction of water sensitive Shales with water in the mud which causes swelling and dispersion of shale (Ni et al., 2016). Hence, shale inhibitors (ranging from former inorganic salts to polymers and recently nanoparticles) are usually added to WBM for elimination or minimization of the shale hydration (An et al., 2015a,b) (see Fig. 2).

#### 4. Additives for drilling

The main component of drilling mud is bentonite which gives it the thixotropic trait and wide range of additives are also added to provide it with essential rheological properties to accomplish well stability and best drilling operation. Such characteristics include plastic viscosity (PV), mud density, yield point (YP), apparent viscosity (AV), lubricity, mud filtrate loss volume as well as gel strength. In addition, this must be combined with proper mud formulation to provide chemical properties that will promote shale inhibition (Aftab et al., 2017).

Bentonite helps in suspension of mud weight material; improve cleaning capacity of mud; provide viscosity; enhance hole stability; and help in the reduction of fluid loss and water seepage into permeable formations by forming thin filter cake with low permeability.

Some common additives in drilling fluids include density control additives, viscosity additives, shale inhibitors, lubricants, flocculants, fluid loss additives (to control loss of drilling fluids into permeable formations) and so on. Extra care is necessary to select additives and their proportion in the mud to obtain best rheological properties (viscosity and density) and others important parameters such as tolerable pH, less corrosivity, thermal stability, and low stickiness. (Bol et al., 1994; Lyons Williams, 1996; Rahman et al., 2000).

### 5. Typical drilling fluids additives

#### 5.1. Additives for viscosity control

Thickeners such as xanthan gum (flowzan), starch, glycol, guar gum, carboxymethylcellulose and polyanionic cellulose (PAC) are the common viscosity additives. This is very vital to achieving the required rheology to support cutting transportation during drilling. However, the reduction of viscosity is accomplished using flocculants. Some of the flocculation additives include brine, potassium chloride, hydrated lime ( $\text{CaCl}_2$ ), acrylates, gypsum ( $\text{CaSO}_4$ ), soda ash ( $\text{Na}_2\text{CO}_3$ ), sodium bicarbonate, tetrasodium pyrophosphate, polyphosphates, and lignosulfates (O'Brien and Chenevert, 1973).

#### 5.2. Density control and filtration control additives

A weighting or density agents such as barite or hematite or calcium carbonate is added to increase the overall density of the drilling fluid. So, sufficient bottom-hole pressure can be maintained thereby preventing any formation damage and facilitates withdrawing of the dry pipe (Shi et al., 2013). Filtration control additives are used to reduce fluid loss of drilling fluid in different mud (either WBM or OBM) and high-temperature drilling condition (Huang et al., 2018a). Example of these additives are carboxy methyl cellulose (CMC), low and high viscosity PAC, bentonite and modified starch in WBM, while gilsonite (asphalt bitumen) and organophilic lignite in OBM. (Lomba et al., 2000).

Although Partially hydrolyzed polyacrylamide (PHPA) can be used to control filtration of drilling fluid, the primary function of PHPA is used to viscosify the drilling fluid and encapsulate the shale particles, i.e. shale encapsulation and thickening (viscosifier) function in drilling mud (O'Brien and Chenevert, 1973; Chen et al., 2003; Wilson and Wilson, 2014). Therefore, PHPA should not be classified as filtration control additives. The WBM filtration control additives roles include hole stabilization and fluid loss minimization predominantly adsorption of water into permeable formations. Gilsonite supports shale formations stabilization, reduces API, high pressure and high temperature (HPHT) fluid loss, and also aid in thermal and emulsion stability and enhance the suspension properties of oil-based fluid systems. (Berthonneau et al., 2017)

#### 5.3. Other additives to shale inhibitors

Other additives being used in drilling fluid are an emulsifier, defoamer. Emulsify agents are anionic, cationic or neutral chemicals that enable a homogeneous mixture of two immiscible liquids. Surfactants, soaps, detergents and organic acids are common emulsifiers in WBM while amine-based compounds and fatty acids are used in OBM (Boek et al., 1995; Wilson and Wilson, 2014). These additives may help in emulsion stability, improve the thermal stability of mud, enhance viscosity and contribute to filtration control (Chen et al., 2003; Spisak, 2011)

Defoamers are chemicals to reduce foaming in mud especially the one for a highly saline environment like brackish and saturated salt water. Other popular additives are the thinning agents which allow the modification of viscosity and the solids content of the fluid. They are used to reduce the thickness to improve fluid permeability (Bol et al., 1994; Huang et al., 2018a; Zhao et al., 2019). An example of such additives is lignosulphonate and lignite. Lubricants and anti-scaling or anti-spotting agents are also widely used as additives in drilling. Their functions are to reduce friction, drag as well as torque in the drilling operation. Stuck pipe free oils, drill detergents, and lube are important substance for lubricity and anti-scaling in muds (Pereira and Pinho, 2002; Mao et al., 2015).



## 6. Inhibitors

### 6.1. Definitions

Inhibitors are materials or chemicals added to water-based drilling fluids to hinder hydration, swelling and degradation of shales and clays (Gholami et al., 2018; Rana et al., 2019). WBM are preferred to oil-based and synthetic-based muds in the case of the environment, reservoir analysis, ECD management, the rate of penetration and safety. Liu and Lu (2006) and Yang et al. (2017) Nevertheless, shale will swell as a result of hydration, dispersed or disintegrated and lead to well instability and mechanical problem without good shale inhibitor. (Chen et al., 2003; Clarkson et al., 2013)

Many drilling fluid additives have been used to either change mud density or its chemical properties to enhance WBM functionality in drilling, especially for shale inhibition (Wilson and Wilson, 2014; Huang et al., 2018b). Additives are either dissolved or suspended in the drilling fluid to increase its density in order to control pressure formation and to combat the effect of sloughing or heaving shales that may be encountered (Yuxiu et al., 2016; Tadros, 2017).

In principle, the negative charges on shale particles are either stabilized by a positive ion of the salts by intercalation in shale matrix and/or shale stabilization due to the formation of hydrogen bond between clay particles and atoms with lone pair atom (N or O) on the polymer used as inhibitors (An et al., 2015a,b; Ni et al., 2016; An and Yu, 2017; Barati et al., 2017; Zhong et al., 2015).

### 6.2. Types of inhibitors

Various chemical inhibitors have been examined in addressing the interaction between water in mud and shales formation, Table 1. Conventional shale inhibitors include inorganic salts of potassium, calcium, and ammonium (KCl, CaCl<sub>2</sub>, NH<sub>4</sub>Cl), asphalt, modified gilsonite, and synthetic or natural polymers. Other inhibitors that have been studied by researchers include polymer of quaternary amines and their salts, ionic and amino acids polymers, glycols, ionic liquids and surfactants (An et al., 2015a,b; Luo et al., 2017).

Traditionally, KCl and potassium salt of partially-hydrolyzed polyacrylamide (PHPA) using KCl are used to diminish the shale swelling difficulties (Lyons Williams, 1996; Liu and Lu, 2006). PHPA may also react with bentonite in low-solid mud, linking its particles together to improve fluid rheology with no consequences of solid laden increment (Aftab et al., 2017). KCl mud efficiency is worthy for shale swelling inhibitions at high concentrations, it has negative impacts on fluid rheology and environment and may result to loss of filtration (Luo et al., 2017; Zhong et al., 2016a,b).

Besides, polymers like acrylamide and PHPA are acceptable heat insulators that can be utilized for inhibition by coating shale surfaces and sealing microfractures with a thin film that retards disintegration and dispersion. This polymer is more effective with the addition of KCl but it does not tolerate the downhole conditions of high-pressure and high temperature (HPHT) (Mao et al., 2015). Amines and imine polymers including their composites of with quaternary ammonium salt and/or other polymers have been reported to be functional inhibitors in previous works (Jiang and Zhang, 2018).

## 7. Nanomaterial as shale inhibitors

Currently, the technical challenges are being faced by gas and oil ad sectors for preparing drilling muds to increase rheological property and shale inhibition to address nanopore throat in shale and withstand high-temperature conditions experienced in the down hole. Rheological properties of the WBM are significant in drilling operation which also serve as an indication of active inhibition of shale (O'Brien and Chenevert, 1973). Conventional WBM contain shale stabilizers and inhibitors as heat insulators, macro or microsize and cannot plug nano-pores of shales.

Thus, water enters into the wellbore resulting in high mud filtrate volume and clay swelling. Expansion and distribution of micro-cracks in hard brittle shale have also shown some concerns in drilling. To deter this, easy formation of filter cake on wellbore by trapping of nanoparticles in pore or micro-cracks to limit filtrate volume by sealing which may lead to enhancement of formation stability (Li et al., 2012; Liu et al., 2017).

Due to low permeability of shale, formation of filter cake via filtration loss on the wall of wellbore is usually difficult. Thus, gradual transfer of equilibrate pressure between mud and pore pressure occurs in the absence of a potential barrier that results into transient pore pressure and instability (Bol et al., 1994). In the presence of microcracks during drilling, filter cake can easily be formed with the cracks playing a major role in filtration loss with less permeation through the material bulk pore throats. Moreover, migration of particle to plug pore throat which actively reduce permeation into formation is experiences at a suitable drilling fluid flow rate (Zhao et al., 2019).

Nanomaterials or nanocomposites have been found to be suitable for effective plugging of microfractures and pore throats due to their ability to reduce fluid loss into cracks and pores of formation. They therefore prevent equilibration between wellbore and pore pressure that could results into formation failure and consequent collapse (Yu et al., 2003).

The effective dispersity of nanomaterials in drilling fluids due to their extremely small sizes enhances their performance to inhibit shale hydration (Yuxiu et al., 2016; Liu et al., 2017; Zhao et al., 2019).

Nanoparticles mud systems have been identified to tackle these challenges. They could enhance fluid rheology (Sharma et al., 2012; Aftab et al., 2017) as well as encourage shale inhibition, lubricity, and filtration of WBM (Sameni et al., 2015). Reports have also shown them to aid mud sealing capacity as plugs for nanopores and micro-fractures in shale drilling, cheap and inexpensive (Li et al., 2012; Pham and Nguyen, 2014; Yang et al., 2015). Nanoparticles could form tough and dense mud cake which may significantly reduce fluid loss (Cai et al., 2012).

Literally, nanoparticles are nanomaterials (1–100 nm size) with the superior surface area and can impact excellent fluid properties at minute concentration (Zhang et al., 2015). They have a distinctive size and hydro-dynamism with the ability to react with formations in inhibiting shale (Amanullah and Al-abdullatif, 2010; Zakaria et al., 2012).

Nanosilica (Hoelscher et al., 2012; Cai et al., 2012; Akhtar-manesh et al., 2013; Mao et al., 2015; Kang et al., 2016; Boul et al., 2017), nanopolymers (Li et al., 2012; An et al., 2015b, 2016), multi-walled carbon nanotube (Aftab et al., 2017), graphene nanoplatelet (Aftab et al., 2017; Yuxiu et al., 2016), laponite (Liu et al., 2017; Huang et al., 2018a); polymer-silica nanoparticles composite (Huang et al., 2018b) among others are typical example of nanomaterials that have been tested as shale inhibitors in water-based drilling fluids with distinguished performance relative to common inhibitors.

**Table 1**

Categories of recent chemical compounds that have been investigated as inhibitors in the water-based drilling fluid.

General categories of inhibitors	Specific inhibitor	Performance comparison	Advantage	Disadvantage	Mechanism	Reference
Amines/amides/imines compounds and polymers	Poly (acrylamide-dimethyldiallyl ammonium chloride/poly (vinyl alcohol)	–	Effective inhibition of shale hydration	Bad odor and cannot withstand high temperature	Electrostatic interaction and hydrogen bonding	<a href="#">Jiang and Zhang (2018)</a>
	Polyethyleneimine	–	”	Degrade at high temperature.	hydrogen bond between -OH on shale particle and amino group on inhibitor	<a href="#">An and Yu (2017)</a>
	Polyamidoamine dendrimers	KCl and Polyetherdiamine (PEDA)	Superior inhibition than conventional KCl and PEDA	Degrade at high temperature.	Hydrogen bonding	<a href="#">Zhong et al. (2015)</a>
	4, 4'-methylenebis-cyclohexanamine (MBCA)	Polyetherdiamine (PEDA)	MBCA is more effective as inhibitor and physical plug of micropores and can withstand high temperature (up to 220 °C) than PEDA	–	Hydrogen bonding	<a href="#">Zhong et al. (2016a)</a>
	Polyetherdiamine (PEDA)	Na and K formate	Efficient inhibition than formate salt	Cannot withstand HTHP	Hydrogen bonding	<a href="#">Zhong et al. (2015)</a>
	Melamine quaternary ammonium salt	–	Excellent inhibition	Toxic and noncompatible with anionic additives	Electrostatic interaction and hydrogen bond	<a href="#">Yu et al. (2017)</a>
	Hydroxyl-terminated polyamidoamine (PAMAM-OH) dendrimers	–	PAMAM-OH retarded shale hydration more effective when combined with KCl	Inhibition maybe minimized at high temperature	Hydrogen bond	<a href="#">Zhong et al. (2016b)</a>
	KCl modified partially hydrophobized hyperbranched polyglycerol (HPG)	Unmodified HPG and commercial PEG400 and polydi-aminedimethyl acrylamide (PDADMAC)	KCl-HPG has superior inhibition than ordinary HPG, PEG400 and PDADMAC.	HPG may undergo degradation at high temperature	Complex formation between HPG and K <sup>+</sup>	<a href="#">Ceraï et al. (2016)</a>
	Polyetheramine (PEA) and poly (vinyl alcohol-g-dimethyl aminopropyl methacrylamide (PVA-g-DMAEMA)	–	Inhibitive characteristic is not affected at high temperature	Expensive	Hydrogen bonding	<a href="#">Shu et al. (2017)</a>
	Polyethyleneimine (PEI)	Chitosan quaternary ammonium salt (HTCC)	PEI is more active inhibitor than HTCC due to positive ion form between water and PEI.	–	PEI nitrogen protonation in water leading to hydrogen bond	<a href="#">Guancheng et al. (2016)</a>
Gelatin	Polyampholyte	–	Inhibit shale swelling effectively	Toxic at high concentration and degrade at relatively high temperature	Ionic interaction and hydrogen bonding	<a href="#">Ma et al. (2017)</a>
	Tallow amine ethoxylate (TAE)	KCl	TAE possesses inhibition compete with that of KCl and it is compatible with other fluid additives	–	Hydrogen bonding	<a href="#">Barati et al. (2017)</a>
	Ethylenediamine-methylacrylate	–	It has good inhibitor property.	–	Hydrogen bonding	<a href="#">Bai et al. (2017)</a>
Gelatin	Gelatin	KCl, PEA, polydimethyldiallyl ammonium chloride (PDMDAAC)	It is biodegradable and has better inhibition than KCl, PEA and PDMDAAC and nontoxic	It may degrade at elevated temperature and requires high quantity in application	Hydrogen bonding	<a href="#">Li et al. (2017)</a>

(continued on next page)

Table 1 (continued).

General categories of inhibitors	Specific inhibitor	Performance comparison	Advantage	Disadvantage	Mechanism	Reference
Graphene	Ethylenediamine-modified graphene (EDA-G)	KCl, polyether amino, and chitosan quaternary ammonium salt (HTCC)	Perform better than KCl and polyether amino but has similar inhibition capacity as HTCC	–	Physical sealing and chemical inhibiting through hydrogen bond formation	<a href="#">Yuxiu et al. (2016)</a>
Ionic liquid	Monomer and homopolymer of 1-vinyl-3-ethylimidazolium bromide (VeiBr)	KCl and HTCC	Effective at low concentration (0.05wt% of VeiBr better than 5wt% KCl but has same functionality as 2wt% PEA). Active at high temperature up to 300 °C .	It might not be compatible with some additives.	Physical plugging and chemically inhibition by hydrogen bonding	<a href="#">Yang et al. (2017)</a>
Natural polymer	Chitosan quaternary ammonium salt (HTCC)	Polyether amino (PEA)	Inhibits shale better than PEA even at high temperature, environmental friendly and biodegradable	It is not compatible with some additives, toxic and pH-dependent	Electrostatic interaction and hydrogen bond	<a href="#">An et al. (2015a)</a>
	<i>Zizyphus spina-christi</i> extract (ZSCE) surfactant	KCl and polyamine	ZSCE has better performance than KCl and the polyamine and it is ecofriendly	Activity may reduce at elevated temperature	Electrostatic interaction and hydrogen bonding	<a href="#">Shadizadeh et al. (2015)</a>
	Triterpenoid saponin from <i>Glycyrrhizin</i> extract of <i>Glycyrrhiza glabra</i>	KCl and t-octylphenoxy polyethoxy ethanol (TX-100)	Biodegradable and environmental friendly and inhibit shale hydration than KCl and TX-100	Degradation may occur at extreme temperature and which would lead to reduction in inhibition	Encapsulation of clay particles by thin film and hydrogen bonding	<a href="#">Moslemizadeh et al. (2017)</a>
	Glucose graft copolyammonium (GGPA)	–	GGPA inhibits water absorption into bentonite efficiently at 0.5 wt% and could withstand temperature around 0–300 °C	Might not be compatible with some additives	Adsorption to clay surface through ion exchange, surface hindrance to water affinity and hydrogen bond	<a href="#">Ni et al. (2016)</a>

### 7.1. Silica-based nanomaterials inhibitors

Akhtarmanesh and co-worker (2013) proved in their work that aqueous colloidal silica performed better than KCl (4 wt%) in Gurpi shale inhibition but majorly at the high amount (10 wt%) ([Akhtarmanesh et al., 2013](#)). The nanoparticles (NPs) which caused a reduction in permeability and pressure increment helped them to accomplish physical plugging. One of the mud formulations used in their examination of the NPs reduced pressure to almost 97% near the wellbore. Fluid penetration into the Gurpi shale was reduced up to 68% compared to KCl saturated solution. Around 35 nm size of NPs was confirmed to give a better result.

[Boul et al. \(2017\)](#) also reported that nanosilicas mud used by their team gave stronger inhibition against shale swelling compared to KCl and silicate muds with superb synergistic interaction with the fluid polymer component (PAC). Especially, when modified with 2-aminoethyl-3-aminopropyltrimethoxysilane (AEAPTS) in both fresh and simulated sea water. The inhibiting mechanism was due to both physical plugging of the pore throats by silica nanoparticles and hydrogen bonding formation with AEAPTS. The image of the functionalized silica is presented in [Fig. 3](#). They concluded that nano silica is compatible with polymers in muds enhanced the inhibitive property especially as an additive in simulated seawater and that maximum performance was sensed in the presence of magnesium and calcium ion. Also, that nano silica mud inhibits shale better than the traditional silicate/KCl muds when compared and that the fluid safe to handle with low

environmental impact due to its low pH (8.5 to 10) compared to silicate muds with pH exceeding 12.

[Yang et al. \(2015\)](#) also formulated a highly efficient nanosilica-based brine mud (NPBMs) that could withstand elevated salinity and temperature roughly 180 °C for drilling a horizontal well to ensure stability. The outcome of their study disclosed that NPBMs had excellent salt tolerance and thermal resistance such that their rheological parameters did not suffer significant fluctuation. The fluid loss of NPBm-1 (containing 4% NaCl and 3%KCl) at 180 °C was only 7.6 mL while that of NPBm-2 (made up of 10% NaCl and 3% KCl) had a fluid loss of 6.6 mL at 150 °C. The muds have excellent lubricity and less water activity which makes them suitable for friction resistance reduction and wellbore stability. They further justified that NPBm-1 could prevent or mitigate pressure spreading from mud into shale to enhance wellbore stability. The previous investigation by the same group showed that silica nanoparticles-based freshwater mud could improve wellbore stability of shale with thermal stability up to 160 °C. The inhibition was based on physical plugging of nanoparticles and compatibility with the inorganic salts, chemical inhibition, and rational drilling mud density which make NPBMs applicable for onshore salt water drilling.

Nanosilica (20 nm) was also tested by [Sharma et al. \(2012\)](#) to inhibit Manco shale and a gas shale swelling in WBM (containing 4% sea salt). They found that the muds were stabled at HTHP and offered a wide range of rheological properties and good lubricity which could make them ideal for lateral drilling operations. They also reported a reduction of shale invasion reduction

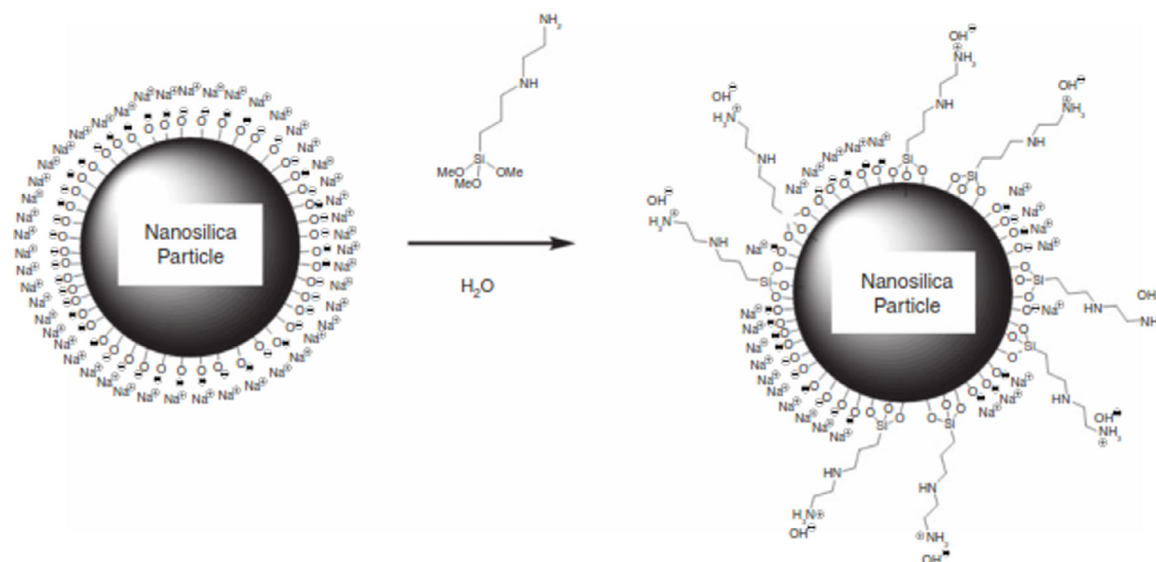


Fig. 3. The functionalized nanosilica-AEAPTS particle with methoxysilane compound (Boul et al., 2017).

Table 2

Typical rheology profile for custom WBM for shale gas (Riley et al., 2012).

Property	Value
Period aged	16
Temperature	150
Fann 35 viscometer data	
600 rpm	120
300 rpm	46
200 rpm	36
100 rpm	24
6 rpm	8
3 rpm	6
10 s	6
10 min	8
PV	28
YP	18

by 10 to 100 times which indicate their viability to minimize instability problems. Sensoy et al. (2009) have previously tested such silica nanoparticles (as received) as an additive in field mud to retard shale permeability of Mexico Gulf Pleistocene shale and Atoka shale by plugging the pores using silica nanoparticles with Stability Temperature of 125 and 170 F. Addition of the silica nanoparticles affected rheological properties (by thinning) of the mud as reported but enhanced the plugging characteristics. Fluid penetration was reduced up to 98% in Atoka shale by the nanoparticle compared to 3% KCl with 16 to 72% and 17 to 27% reduction in fluid penetration were recorded in Atoka shale and Gulf of Mexico shale respectively. Reduction of nanoparticles concentration below 10 wt% was affirmed to retard plugging in Atoka shale under the used tests conditions. The best sealing performance was achieved in their study with 20 nm particle than 5 nm as observed in Fig. 4.

As reported by Riley et al. (2012), silica nanoparticles usually require different suspension packages. They said that the surfactant-based suspension package can have a significant impact on fluid rheology leading to gel spacing or syneresis.

The better pugging effect was noted by increasing the concentration of the nanoparticle in custom WBM (properties in Table 2) when the permeability test was carried out on the studied shale. The bottom fluid pressure improved owing to fluid transmission across the shales and equilibrated with the pressure of top driving after 10 h with 250 psi pressure differential when

tested with 4% NaCl solution having similar water activity. However, when nanosilica was added to replace brine, there was no pressure transmission after 25 h at 250 psi pressure differential with permeability reduction of 97.6% compared to 77.1% achieved by the WBM. After this, when the 4% NaCl solution was then tested repeatedly, there was no bottom pressure transmission recorded which confirmed the achievement of physical plugging by nanoparticles (with 97.6% permeability reduction). The nanosilica contained WBM was also proved to seal 35  $\mu$ m fracture in Texas shale and displayed synergic effects with the presence of large fractures (Riley et al., 2012).

The same nanoparticle used by Riley et al. (2012) was also tested for Macos shale by Ji et al. (2012). They concluded that water invasion could be reduced or completely shut off by water-based drilling fluid that contains nanosilica through physical plugging of pores and microfractures to inhibit shale. They further justified that nanoparticles can only plug pores alone effectively but not microfractures and that combination of well-formulated drilling fluid and concentration of nanoparticles is key to shield water invasion into shale with or without microfracture.

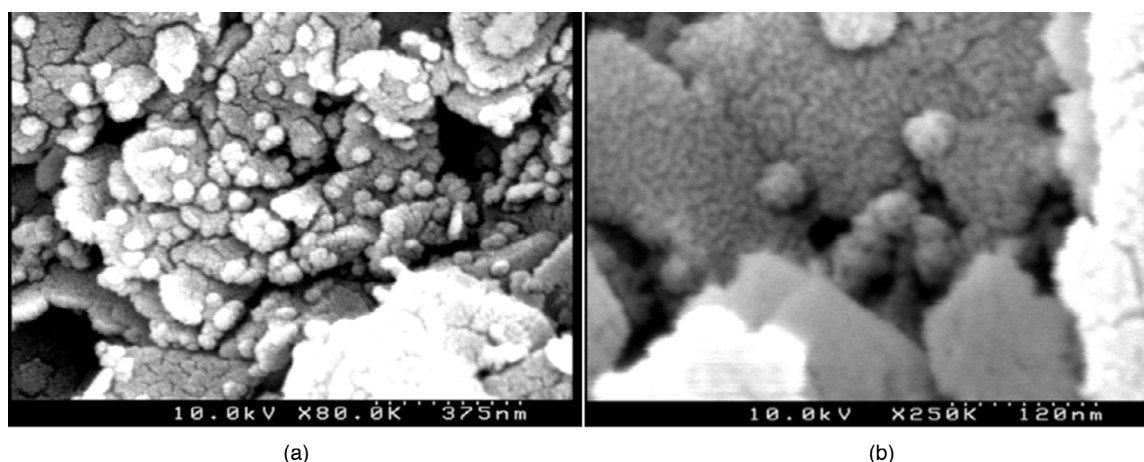
Pham and Nguyen (2014) demonstrated the effect of polyethylene glycol (PEG)-coated silica nanoparticles on clay swelling and aqueous stability of nanoparticle dispersions. The authors make the following conclusion from their study. The reported nanoparticles inhibit clay swelling when NaCl and KCl were added in a synergistic way. The addition of nanoparticles to fluids containing electrolyte resulted in a more decrease in the swelling index. Comparing with NaCl or KCl-containing muds, it showed better inhibition. The swelling index reduced by increasing the amount of electrolyte.

The addition of the polymer-coated silica nanomaterials reduced swelling indices for the reported concentrations of the nanomaterials compared. Nevertheless, the reduction between swelling indices moderated with the increase in both electrolyte and nanomaterials. The fluid pH was reported to have little effect while temperature has a significant effect. The swelling index was reported to be more at 70 °C compared to 25 °C which makes it to be viable at high temperature and high pressure.

## 7.2. Carbon-based nanomaterials inhibitors

Ethylenediamine-modified graphene (EDA-G) has been suggested to have the ability to plug nanopores formation with a





**Fig. 4.** (a) SEM of 20 nm particles with Atoka shale, (b) The aggregate of particles plugging a pore throat (Sensoy et al., 2009).

**Table 3**

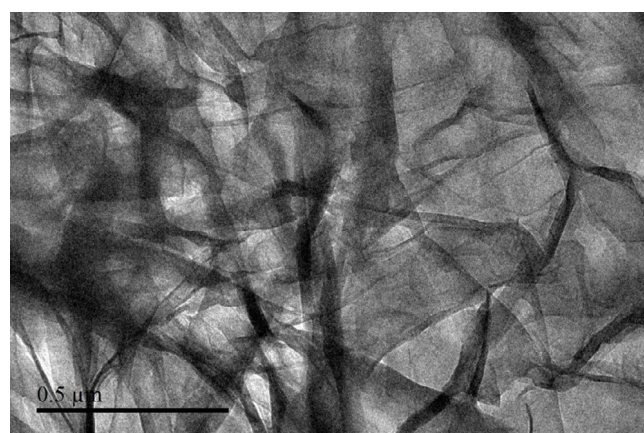
Formulation of drilling muds (Aftab et al., 2017).

Materials	KCl/PHPA WBM	Basic WBM	Nanosilica WBM	GNP WBM	MWCNT WBM	Mixing time
Fresh water (ml)	195	195	195	195	195	–
KCl (ppb)	34.1	11.3	11.3	11.3	11.3	3
NaOH (ppb)	0.2	0.4	0.4	0.4	0.4	2
Flowzan (ppb)	0.3	0.6	0.6	0.6	0.6	5
PAC (ppb)	3.7	3.7	3.7	3.7	3.7	5
PHPA (ppb)	7	–	–	–	–	10
Barite (ppb)	200	200	200	200	200	30
Nanosilica (ppb)	–	–	0.1	–	–	5
GNP (ppb)	–	–	–	0.1	–	5
MWCNT (ppb)	–	–	–	–	0.1	5

low volume of filtration and it has been confirmed in achieving high inhibitive performance at low carbon content (0.2 wt%) than other materials examined (Yuxiu et al., 2016). Graphene nanoplatelet (GNP) rheological and shale inhibition characteristics have also been justified to surpass that of KCl/partially hydrolytic polyacrylamide (PHPA) which in turn showed better performance than nanosilica and multi-walled carbon nanotube and commercial KCl (Aftab et al., 2017). Yuxiu et al. (2016) established the ethylenediamine-graphene (EDA-G) gave good efficiency to plug nanopores of the shale formation. The performance of these particles was compared to some other nanomaterials including graphene oxide (GO), nanosilica, amino silica, zinc oxide, and graphite. Fig. 5 shows the TEM image of GO as an example.

Linear swelling tests using bentonite indicated that adding water, KCl, polyether amino, chitosan quaternary ammonium salt (HTCC) and EDA-G reduced the expansion height by 47%, 57%, 62%, and 62%.

The rheological properties and shale inhibition behavior of water-based mud using graphene nanoplatelet (GNP) less than 0.1–2  $\mu\text{m}$  in size, nano-silica and multiwalled carbon nanotube (MWCNT) have also been compared by Aftab et al. (2017). Table 3 shows the formulation of the nanoparticle-containing drilling



**Fig. 5.** TEM image of GO as an example.

fluid tested. As can be seen on Table 4, there was no significant variation between the base WBM and the nanoparticles-WBM. Among the nanoparticles-WBM tried to retard shale swelling, GNP demonstrated the maximum effective result.

### 7.3. Other nanoparticles shale inhibitors

Vegard and Belayneh (2017) studied the effect of Titanium Nitride (TiN) nanoparticle (NPs) with an average size of 20 nm in polymer (CMC) and salt (KCl) treated bentonite drilling fluid systems at 22, 50 and 70 °C temperatures. They concluded that the addition of 0.0095 wt% TiN-NPs reduced the friction coefficient of the conventional nano-free drilling fluid by an average of 46%. Also, the yield stress and plastic viscosity increased significantly by 122% and by 17%, respectively, and the API filtrate loss decreased by 7.1%. The torque and drag simulation results show that the friction coefficient reduction increased the drilling depth

**Table 4**

Rheological properties and filtrate volume (API and HPHT) (Aftab et al., 2017).

Drilling muds	PV (mPa s)	YP (Pa)	10-s GS, (Pa)	10-min. GS, (Pa)	CoF	API FL (ml)	HPHT FL (ml)
WBM	22	13	4.5	5	0.2	6	16
WBM + MWCNT 0.1 ppb, KCl 11 ppb	23	14	4.5	5	0.1	5.6	15
WBM + Nanosilica 0.1 ppb, KCl 11 ppb	21	12	4.5	5	0.2	5.8	17
WBM + GNP 0.1 ppb, KCl 11 ppb	23	14	4.5	5	0.1	5.5	14
WBM + KCl + PHPA KCl 34 ppb, PHPA	24	15	5	5.5	0.2	5.5	15
3 ppb							

**Table 5**

Performance of different nanomaterials that have been tested as inhibitor in WBM.

Categories of materials	Specific inhibitor	Performance comparison	Advantage	Disadvantage	Mechanism	Reference
Nanosilica	Colloidal silica (35 nm)	KCl (4 wt%)	Better performance and fluid penetration (68%) than KCl.	High quantity required (10 wt%)	Physical plugging	<a href="#">Akhtarmanesh et al. (2013)</a>
	Polyethylene glycol (PEG) coated silica nanoparticles	NaCl or KCl-containing mud	Better activity when combined with either KCl or NaCl and the effect of fluid pH is negligible.	It is sensitive to temperature. Swelling index is more at 75 °C than 25 °C but no clear different between 55 °C and 50 °C swelling.	Physical plugging and hydrogen bonding formation with OH groups on PEG	<a href="#">Pham and Nguyen (2014)</a>
	Nanosilica modified with 2-aminoethyl-3aminopropyltri methoxysilane (AEAPTS)	KCl and silicate muds	More effective than KCl and silicate especially in the presence of calcium and calcium ions and when combined with PAC. Low environmental impact and save handling due to low pH (8.5–10) than silicates (pH > 12).	–	Physical plugging of pore throat and hydrogen bonding formation with AEAPTS	<a href="#">Boul et al. (2017)</a>
	Nanosilica-based brine mud (NPBMs)	–	Ability to stabilizes horizontal well and tolerate elevated temperature (up to 180 °C) and salinity	–	Physical plugging	<a href="#">Yang et al. (2015)</a>
	Nanosilica (20 nm)		Reduction of shale invasion reduction by 10 to 100 times in 4% sea salt WBM. It can withstand HTHP and suitable for the stabilization lateral well drilling.	–	Physical plugging	<a href="#">Sharma et al. (2012)</a>
	Nanosilica (20 nm)	3% KCl	Silica nanoparticles (<10 wt%) retarded fluid penetration (98%) in Atoka shale compared to 3% KCl with 16 to 72% and 17 to 27% in Atoka shale and Gulf of Mexico shale respectively. It is effective up to 77 °C in a mud with salt concentration of 4 wt%.	High quantity required (10 wt%) and mud rheology significantly affected.	Physical plugging	<a href="#">Sensoy et al. (2009)</a>
	Nanosilica	NaCl mud	Permeability reduction of 97.6% compared to 77.1% of WBM for active sealing of Texas shale (35 µm fracture)	High amount (29 wt%) was used.	Physical plugging	<a href="#">Riley et al. (2012)</a>
	Commercial silica (5–100 nm)	Brine, CaCl <sub>2</sub> and KCl mud	It reduces fluid loss significantly and no change in silica solution properties in the presence of NaCl.	It solidifies in the presence of sodium hydroxide.	Physical plugging	<a href="#">Hoelscher et al. (2012)</a>
	Silica nanoparticle in water-based drilling fluids (WBDFs)	Oil based drilling fluids (OBDFs)	Silica nanoparticles significantly enhance inhibition and reduces swelling rate and filtration loss in WBDFs because it easily disperse in WBDFs.	Silica nanoparticles fail to reduce invasion damage in OBDFs due to poor dispersion of nanosilica in OBDFs. High amount is usually needed (close to 10 wt%)	Physical plugging	<a href="#">Kang et al. (2016)</a>
Carbon-based	Ethylenediamine-modified graphene (EDA-G)	Graphene oxide (GO), nanosilica, amino silica, zinc oxide, and graphite	Performed more than other materials at low carbon content (0.4 wt%)	–	Physical plugging and hydrogen bonding with EDA	<a href="#">Yuxiu et al. (2016)</a>
	Graphene nanoplatelet (GNP)	KCl/partially hydrolytic polyacrylamide (PHPA), nanosilica, multi-walled carbon nanotube and KCl	GNP is more active than other materials compared	–	Physical plugging	<a href="#">Aftab et al. (2017)</a>
Polymer and polymer composites	Nanoflexible polymer	Common fluid loss agent (PAC)	Polymer do not change mud viscosity upon added, but reduces fluid loss more than convectional fluid loss agent.	–	Physical plugging	<a href="#">An et al. (2016)</a>

(continued on next page)

Table 5 (continued).

Categories of materials	Specific inhibitor	Performance comparison	Advantage	Disadvantage	Mechanism	Reference
	Nano terpolymer of acrylamide - 2-acrylamido-2-methyl -1-propane sulfonic acid - N-vinyl-pyrrolidone (AM-AMPS-NVP)	PAC	The nano AM-AMPS-NVP terpolymer give better fluid loss reduction at in high salinity, calcium and high temperature than PAC.	–	Physical plugging	An et al. (2015b)
	Polyacrylamide-grafted-polyethylene glycol/SiO <sub>2</sub> nanocomposite	partially hydrolyzed polyacrylamide (PHPA) polymer	Compatible with other additives used mud system with suitable filtration and rheological properties. It exhibits high thermal (up to 95 °C) and salinity stability, high shale recovery as well low formation damage than PHPA	–	Physical plugging and hydrogen bonding	Jain et al. (2015)
	Hydrophobic polymer based silica nanoparticles composite with center core	PHPA	The composite fluid has good lubricity, rheology, high thermal stability and low fluid loss. Effective to plug formation, even under high salinity.		Physical plugging, hydrogen bonding and water repulsion by styrene chain.	Mao et al. (2015)
	Acrylic resin/nano-SiO <sub>2</sub> composite (AR/SiO <sub>2</sub> )	–	Mud (with 1 wt% AR/SiO <sub>2</sub> ) plug shale pore efficiently by with better filtration properties and improve wellbore stability by reducing fluid invasion. Ability to with extreme temperature (up to 250 °C)	–	Physical plugging due to excellent adhesion of deformable core shell of AR/SiO <sub>2</sub> with shale matrix.	Huang et al. (2018b)
Other nanoparticles	Titanium Nitride nanoparticles (TiN-NPs) in CMC and KCl	CMC and KCl mud	Addition of 0.01 wt% TiN-NPs in CMC decreases filtration loss by 7.1%.		Physical plugging	Vegard and Belayneh (2017)
	Laponite nanoparticles	2% nano-SiO <sub>2</sub> and 4% Na-BT	It displayed brilliant rheological, plug nano-cracks and decreases shale swelling at low quantity (2 wt%). It forms smoother and compact filtrate cake that reduces water invasion into formation than sodium bentonite.	–	Physical plugging of nanopores.	Liu et al. (2017)

by +31% compared to the nano-free system (Vegard and Belayneh, 2017).

The performance of nano-TiN in CMC was compared with nano-free systems. It was reported that for the nano-TiN additive systems, the measured rheology values are higher than the nano-free system. The responses of the 0.05 gm and 0.1 gm are nearly the same and are higher than the rest of the drilling fluids (Vegard and Belayneh, 2017). According to a study conducted by Li et al. (2012), the pore sizes of most shale samples were less than 1 µm while most drilling fluid have large particles sizes more than pore throat (range from 0.1 to 100 microns). Their team reported that sized calcium carbonate generally used as an effective bridging agent for sealing pore throat in porous and permeable formations but are not suitable for small throat shale compared to nanoparticles. The nano additive used in their study (not mentioned) when added to base fluid displayed better inhibitive character against the shale tested with retardation in pressure transmission of shale compared to calcium carbonate.

Nano flexible polymer mud have also been used to reduce surface area, pore size and pore volume of shale core sample. Only nanosized pores were plugged by polymer molecules by forming film coating on the rock surface (An et al., 2016). Detail information of sequence nanomaterials that had been investigated in addressing formation invasion and damage are presented in Table 5.

## 8. Conclusion and future perspective

Current investigations have a clear justification on the efficacy of nanomaterials to appreciably suppress shale swelling and dispersion connected with water-based drilling fluids. Nanoparticles based drilling fluids have the potential to significantly reduce drilling and disposal cost with significant environmental advantage. Hence, they could be suitably applied for drilling long lateral sections in shales and tight gas reservoirs which usually involve huge capital cost. Further discovery of cheap and sustainable nanomaterial as shale inhibiting agents are needed for the effective reduction of wellbore problems even at high temperature and high pressure in the downhole. The core emphasis of current research is the development of biodegradable materials and nanomaterials that can be broken down by organisms such as earthworm or microbes. On the other hand, components of drilling fluid wastes can also be employed for the fertilization of soil. The idea behind the development of environment-friendly shale inhibitors is to develop a system that can be beneficial for the environment. Therefore, selection of each component of the drilling fluid such as base fluid, emulsifier, internal phase, a weight material, and fluid loss additives is highly crucial. Time demands to develop an environmentally friendly shale inhibitor. The uncontrolled exploration of oil and gas in environmentally sensitive areas can produce an irreversible effect on the surroundings. The nanoparticles-based shale inhibitor can be developed by a proper understanding of the fundamentals of clay swelling and mechanism of shale inhibition. When nanoparticles are proposed

as shale inhibitors, it is necessary (i) to ensure the dispersion stability of nanoparticles in drilling fluid under HTHP environment, (ii) to find out how the nanomaterials stabilize shale, and (iii) to know what kinds of experiments are suitable to evaluate the performance of nanomaterials in stabilizing shale.

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