Review Article

A REVIEW OF NANOTECHNOLOGY APPLICATIONS IN THE OIL AND GAS INDUSTRIES

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Abstract

Nanotechnology encompasses the science and technology of objects with sizes ranging from 1 nm to 100 nm. Today, exploration and production from conventional oil and gas wells have reached a stage of depletion. Newer technologies have been developed to address this problem. Maximum oil production at a minimum cost is currently a huge challenge. This paper reviews nanotechnology applications in the oil and gas production sector, including in the fields of exploration, drilling, production, and waste management in oil fields, as well as their environmental concerns. The paper reviews experimental observations carried out by various researchers in these fields. The effect of various nanoparticles, such as titanium oxide, magnesium oxide, zinc oxide, copper oxide, and carbon nanotubes in drilling fluids and silica nanoparticles in enhanced oil recovery, has been observed and studied. This paper gives a detailed review of the benefits of nanotechnology in oil exploration and production. The fusion of nanotechnology and petroleum technology can result in great benefits. The physics and chemistry of nanoparticles and nanostructures are very new to petroleum technology. Due to the greater risk associated with adapting new technology, nanotechnology has been slow to gain widespread acceptance in the oil and gas industries. However, the current economic conditions have become a driving force for newer technologies.

Keywords: Nanoparticles, drilling fluids, wettability, enhanced oil recovery, density, rheological properties.

1. Introduction

The concept of nanotechnology was first introduced by the renowned physicist Richard Feynman in 1959 in his talk "There's Plenty of Room at the Bottom." He discussed the possibility of the synthesis of nanoparticles via the direct manipulation of atoms. For the past few decades, nanotechnology has had various applications in food, medicine, electronics, and cosmetics. These tiny particles have exceptional characteristics that have proven to be of fundamental importance in various fields. Manufactured nanoparticles are considered to be very effective for various uses in oil and gas drilling and related industries due to their extraordinary physical and chemical properties at the nanometer scale. Structured nanoparticles can help in structural strength enhance-ment, energy conservation, and overcoming the technical and environmental challenges faced during drilling and production operations. Nanoparticles have various applications in exploration, reservoir, drilling, and production operations. Nanotechnology is characterized by collaborations between various diverse disciplines, which makes it innovative and more precise than other technologies. It can contribute to creating more efficient, cost effective, and environmentally friendly technologies than other available technologies. Nanotechnology enhanced materials provide strength and endurance to increase reliability in drilling and improve the drilling performance in high pressure to high temperature (HPHT) environments. Such technology can also improve the hydrophobic or hydrophilic behavior of materials and therefore enhance materials for water flood applications [1]. Nanoparticles have a high surface area to volume ratio. Due to this, their interactions

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with their surroundings are more effective and give better results than other conventional additives that are generally used today in the oil and gas industries. Exploration and production in HPHT environments pose a great challenge today because most additives, such as polymers, start deteriorating at high temperatures and their properties change. Today, maximum production using optimum concentrations of additives from depleted reservoirs requires new and innovative technologies such as nanotechnology. Even though the cost of nanoparticles is very high, they can very effectively increase oil production and decrease the overall drilling cost. The benefits oil industries will reap due to the application of nanotechnology are enormous; even though the initial cost will be high, the overall cost will be low because nanoparticles can replace most of the additives used today and a very small amount of nanoparticles can be very effective. This is studied in detail in this paper. Nanomaterials are classified based on their origins, dimensions, and structural configurations [2]. On the basis of their origin, they are classified into natural nanomaterials and artificial nanomaterials. Natural nanomaterials are derived directly from natural Earth resources. Artificial nanomaterials are synthesized in various experiments. There are four basic types of artificial nanomaterials: carbon based, metal based, dendrimers, and composites. On the basis of their dimensions, nanomaterials are classified into zero dimensional (0D), one dimensional, two dimensional, and three dimensional (3D). Nanomaterials that have nano dimensions in all three directions are called 0D nanomaterials.

The measurement and characterization of nanoparticles pose interesting analytical challenges. The characterization of nanoparticles is based on the size, morphology, and surface charge of the nanoparticles. Advanced techniques are used for such characterizations, including atomic force microscopy (AFM), scanning electron microscope (SEM), transmission electron microscope (TEM), X ray photoelectron spectroscopy, mass spectrometry, atomic emission spectroscopy, and ion chromatography [3]. The particle size can be determined using a particle size analyzer, which determines the diameter of the particles. Such an instrument can show the average sizes of the particles to determine if nanoparticles have been formed; this is one of the preliminary steps in nanoparticle studies. The surface area of a nanoparticle can be determined via nitrogen adsorption using the Brunauer Emmett Teller (BET) method. The interaction of nitrogen with solids is very strong. In this method, nitrogen gas is released stepwise inside a sample cell. A partial vacuum is created to maintain a relative pressure that is less than the atmospheric pressure. No further adsorption occurs after the saturation point is reached. Then, the sample is removed from the nitrogen atmosphere after the adsorption layers have formed. Isotherms of the amount of gas adsorbed as a function of the relative pressure are then collected and displayed in the form of a BET isotherm [4]. Surface techniques such as X-ray photoelectron spectroscopy and secondary ion mass spectrometry are generally used to determine the composition. Mass spectrometry, atomic emission spectroscopy, and ion chromatography are a few bulk techniques that can also be used. SEM is generally used to measure properties such as the surface topography and composition and for raster imaging. This technique determines the size, shape, and surface morphology via a direct visualization of the nanoparticles. In this method, the solution containing the nanoparticles is initially converted into a dry powder. This dry powder is then mounted on a sample holder. A focused fine beam of electrons is then used to study the sample [5]. Secondary electrons, which are emitted from the sample surface, help determine the surface characteristics of the sample [6]. TEM is used to determine the shape and size of the particles. When the crystalline sample interacts with the electron beam (primarily via diffraction rather than absorption), a high contrast image is formed by blocking the deflected electrons, which contain information concerning the crystal structure. This can generate both bright or light field and dark field images. Jamal Nasser et al., has synthesized nanomud by mixing nanographite and nanowires. SEM and XRD images of nanographites and TEM images of nanowires has been shown in Figures 1–3 [7].

**Table 1.** Advantages and disadvantages of SEM and TEM

Advantages of TEM over SEM	Advantages of SEM over TEM
TEM can produce images that have higher magnification and greater resolution than images produced by SEM. Samples for TEM can be magnified by more than 50 million times whereas in SEM it is limited to 1 to 2 million times. It provides information on the inner structure of the sample like crystal structure, morphology, stress state information etc.	Preparation of samples is easier for SEM as compared to TEM. Study of surface morphology can easily be carried out using SEM. Three dimensional images are possible for SEM whereas TEM provides only two dimensional images of inner structure which complicates its analysis at times.
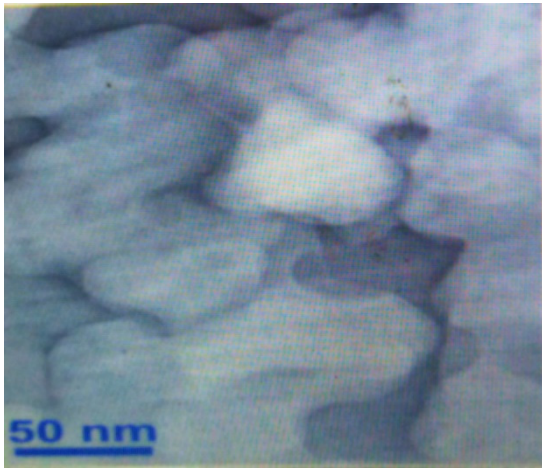
Fig. 1. TEM imaging of nanographite [7].
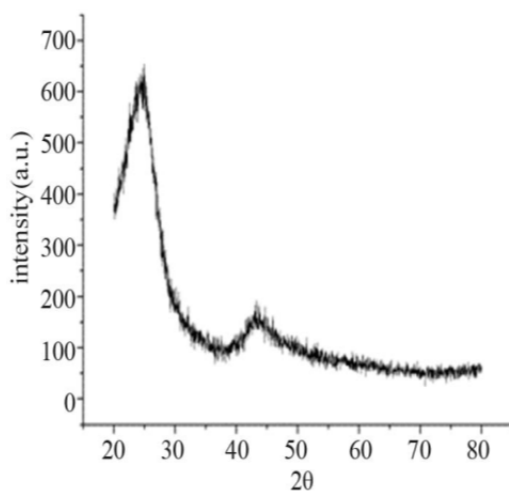
Fig. 2. X raydiffraction pattern of nanographite [7].
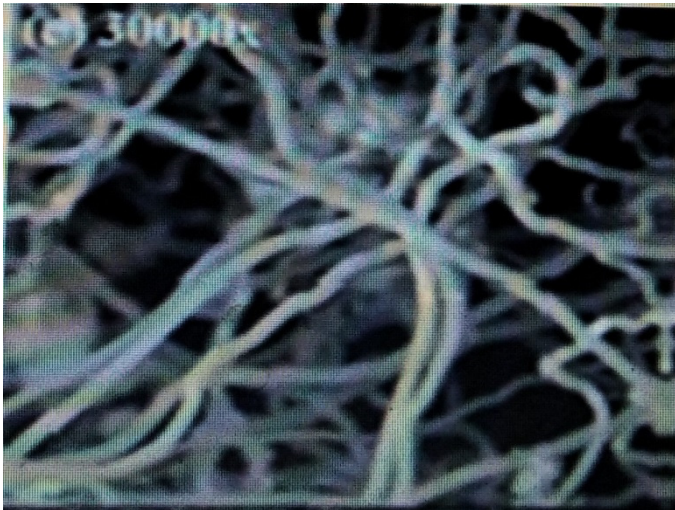
Fig. 3. SEM imaging of silicon nanowires [7].

AFM is used to determine the morphology, the texture of the surface, and the roughness of the particles. It offers 3D visualization capabilities, and both qualitative and quantitative information can be obtained. Information such as the surface area, volume distribution, and size can also be determined.

2. Applications of Nanotechnology in the Oil and Gas Industries

Petroleum industries today are trying to reap the benefits of nanotechnology, be it in the fields of exploration, production, or refining. Nanofluids in oil and gas field applications are defined herein as drilling, drill in, completion, stimulation, or any other fluids used in the exploration and exploitation of oil and gas that have at least one additive whose particle size varies between 1 nm and 100 nm [8, 9].

2.1. Exploration

The use of nanosensors by petroleum geoscientists during exploration is widely seen today [10]. Because nanoparticles behave differently from their bulk counterparts with respect to their magnetic, optical, and electrical properties, imaging contrast agents and sensors can easily be developed for nanoparticles [11]. A special type of sensor called nano dust can be placed in the pore space for various purposes during exploration, including fluid type recognition, fluid flow monitoring, and reservoir characterization [12]. It has been found that micro computerized tomography cannot effectively detect the pore structure of tight formations. Therefore, to obtain insight concerning such information, nano tcomputerized tomography can be used [13].

Liu He et al [14] studied the application and prospects of nanotechnology in oil exploration. Nano characterization technology can be used to determine the mineral composition and micropore structure, to analyze the organic components, and to provide in situ characterizations of reservoirs. Seepage mechanisms of unconventional oil and gas can be studied in detail due to the development of digital core technology, which will further help in the prediction of oil and gas developments in the future [14–18]. A new technology called nanoelectromechanic systems has also been developed. This type of micro module integrates the excellent properties of nanomaterials, and its nano size allows it to move into the micropores of reservoirs. Nanoelectromechanic technology, when combined with the demand of the petroleum industry, will likely result in great benefits. Nano sensing devices, which are made using advanced nanoparticles such as graphene, carbon nanotubes, magnetic nanoparticles, and piezoelectric materials, are injected into reservoirs for reservoir parameter characterization [19]. The electric, magnetic, and acoustic behaviors of reservoirs can be

improved by injecting nano developers and nano signals. Accordingly, information such as the reservoir porosity, permeability, and oil saturation can be obtained more accurately. America Advanced Energy Consortium has investigated the effect of the loading migration of magnetic nanoparticles in the fluids of porous media and has experimentally investigated the distribution of nanoparticles in porous media using physical simulations [14]. Agenet et al [20] prepared fluorescence nanoparticles for intelligent fluid tracing. In addition, paramagnetic nanofluids have been prepared and the migration laws of magnetic particles in porous media have been studied using simulations [21]. Reservoir nanorobots have been developed by Saudi Aramco. These nanorobots are reservoir detection devices that integrate a reservoir sensor, a micro to dynamic system, and a micro signal transmission system. They were tested successfully for the first time in June 2010 and have proved very useful for real time recordings and storing and transferring data and information such as the reservoir temperature and pressure, the pore morphology, and the fluid type and viscosity. They have a high recovery ratio, stability, and mobility. Further, it has been observed that the spatial resolution of reservoir nanorobot detection technology is much higher than that of seismic, logging, and 3D core scanning analyses [22].

2.2. Production

In the production phase, nanotechnology is used for hydrate recovery. The recovery of hydrate can be improved if the water cage decomposes and releases the hydrocarbon (methane). This is achieved by injecting nickel iron nanoparticles into the hydrate formation [23]. During stimulations, high molecular weight cross linked polymers are widely used; however, they produce large amounts of residue. Consequently, researchers are studying the effect of low molecular weight surfactants as fracturing fluids with nanoparticles [24]. Efficient stimulation operations can easily be performed because nanoparticles give the desired properties to the fracturing fluid. Nanoparticles can develop a hydrophobic surface inside the production tubing. This helps reduce scale deposition inside the tubing [25].

2.2.1. Enhanced oil recovery

The use of silica nanoparticles for remobilizing oil in a heterogeneous carbonate reservoir rock has been demonstrated by Pak et al. [26]. They used four dimensional (time resolved 3D) imaging at the pore scale using the X ray computed micro tomography technique where the captured 3D tomographic time series data reveal the dynamics of the immiscible oil displacement via nanoparticle suspensions in the carbonate reservoir rock.

An optimized nanoparticle enhanced oil removal process was designed by studying the nanofluid oil interfacial tension (IFT), the particle retention for a nanoparticle to rock pair, and the nanoparticle suspension stability over time [26]. Hydrophilic silica nanoparticles decreased the IFT with increasing nanoparticle concentration, as shown in Figure 4. The water wet carbonate reservoir was flooded with a suitable slug of silica nanofluid. A two phase flow experiment was conducted including primary drainage, an imbibition (water displacing oil and water flooding), and two subsequent nanofluid injections. A 3D volumetric image of the rock was taken after each injection. It was observed that, due to the injection of the nanofluid, the local fluid distribution along the core length changed and therefore the oil that was trapped at the end of the water flooding was remobilized by the nanofluid. It was further observed that the adsorption of nanoparticles at the fluid fluid interface causes the nanofluid oil IFT to decrease with increasing nanoparticle concentration [27, 28].
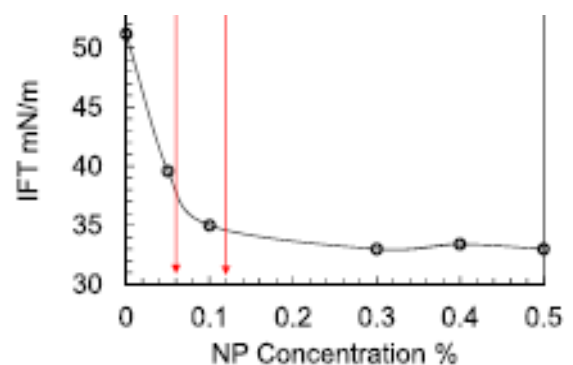
Fig. 4. IFT (oil nanofluid) concentration as a function of the nanoparticle (NP) concentration.

Nanoparticles have a strong effect on the interfacial tension. Zargartalebi et al. used silicon oxide nanoparticles for enhanced oil recovery [29, 30]. The synergistic effect of silicon oxide nanoparticles and cationic surfactants on the IFT has also been investigated [31]. It was observed that the nanoparticles lowered the IFT because the cationic surfactant altered the surface of the nanoparticles from fully hydrophilic to partially hydrophobic. The effect of

silicon nanoparticles and anionic surfactants was also studied by Ma et al. [32], who found that the addition of hydrophilic silicon oxide nanoparticles enhances the efficacy of anionic surfactants when reducing the IFT. However, hydrophilic silicon oxide particles have no influence on the performance of nonionic surfactants [32].

A study of the impact zirconium dioxide on the interfacial properties of anionic surfactants revealed that nanoparticles augment the surface activity of anionic surfactants and lower the IFT between water and oil [33]. The effects of aluminum oxide, iron oxide, and silicon oxide on the IFT were also studied by Joonaki and Ghanaatian [34]. They found that increasing the concentration of nanoparticles causes the IFT to decrease. Silicon oxide nanoparticles were found to be more efficient at reducing the IFT between water and oil. Therefore, the IFT can be reduced using nanoparticles either alone or in combination with surfactants. Moreover, nanoparticles can also reduce the adsorption of surfactants on the reservoir rock surface.

Babadagli et al. studied the dynamics of capillarity imbibition. Static imbibition experiments were conducted on oil and water wet rock samples under different boundary conditions and saturated with different types of oil. The capillary imbibition rate, ultimate oil recovery, and shape of the recovery profile were analyzed, and it was concluded that the reduction in the IFT between the aqueous phase and the oil is the main cause of higher oil recovery [35, 36].

The biggest advantage of nanoparticles, which improve the recovery to a great extent, is their small size. Due to their high surface area, the rate of chemical diffusion is very high. This helps increase their penetration into reservoirs and effectively improves the injection. Due to the high surface area, more active sites are present on the surfaces of the nanoparticles, which helps form stronger bonds with the media. This also increases the stabilization [37].

2.2.2. Wettability alteration

Many researchers have reported results on wettability alterations using nanoparticles either alone or in combination with surfactants. The wettability alteration using nanoparticles depends on several factors, such as the nature of the nanoparticles, the hydrophobicity, the nature of the reservoir, and the nanoparticle concentration.

It is known from waterwet reservoirs that the oil recovery rate is high and becomes lower as the rock becomes increasingly oil wet. In terms of the wettability of a rock, nanoparticles play a major role because they can change the wettability of a rock from oil wet to water wet. In addition, they can also strengthen the wettability of a water wet rock [38]. Silicon oxide nanoparticles were found to be efficient in altering the permeability. Moradi et al. found that silicon oxide nanoparticles alter the wettability of carbonate rock by adsorbing on the surface [39]. The wettability alteration due to multi walled carbon nanotube (MWCNT) silicon oxide nanofluids have been also been investigated for different rock samples.

Benjomea et al [40] designed nanofluids of different concentrations ranging from 10 ppm to 10,000 ppm by dispersing alumina nanoparticles in an anionic surfactant. The wettability alteration was studied via the contact angle and imbibition tests. They observed that the nanofluids changed the wettability of the sandstone cores from the oil wet to water wet condition. The nanoparticles helped enhance the imbibition process and restore the original core wettability. It was also observed that the nanoparticles increased the efficiency of anionic surfactants as a wettability modifier in concentrations lower than or equal to 500 ppm [40]. Wettability alterations in carbonate reservoirs have also been studied by Abhishek et al. [41]. The effectiveness of nanofluids consisting of silane coated silica nanoparticles as in situ reservoir agents was investigated, and they concluded that the nanoparticles change the wettability to a more water wet state and have potential for enhanced oil recovery in carbonate reservoirs [41]. Li et al. [28] conducted a series of core flooding experiments with nanoparticle fluids (nanofluids) as a tertiary recovery method. The effect of the wettability alteration due to injecting a nanofluid into Berea Sandstone samples was shown. It was observed that flooding the core samples using colloidal nanoparticles did not affect the pressure drop; however, the pressure drop increased significantly when using nanostructure particles. The nanofluids helped change the core to a more water wet condition. Further, it was concluded that the increase in the wettability index is independent of the nanoparticle concentration.

2.3. Refinery and processing

Because nanoparticles can extract harmful gases such as sulfur dioxides, nitrogen oxides, and acids from vapor, they are widely used in refining and

processing. Nanomembranes have been used to separate gas streams and to remove impurities from oil [42]. The upgradation of heavy oil and bitumen can be performed onsite using nanocatalysts so that the need to transport and handle these materials can be avoided [43].

2.4. Drilling and completion

Due to their larger surface area, nanoparticles enhance the quality of the base drilling fluid because they are chemically more active. The strength, electrical, and thermal properties can therefore be improved. Various nano to based drilling fluids can be synthesized using a blend of several commercial nanomaterials and nanostabilizers to create desirable rheological and filtration properties as well as a good mudcake quality [44].

Nanoparticles in drilling fluids can be used to combat the multiple drilling challenges discussed in the following subsections.

2.4.1. Improvement in the rheological properties of the drilling fluid

To determine the drilling mud efficiency, it is very important to study the rheological properties of the mud. The rheological properties include the plastic viscosity, yield point, and gel strength. The rheological properties are also very important to determine whether the mud is minimizing the borehole erosion, how effective it is in increasing the rate of penetration, and the compatibility of the mud with the borehole and logging equipment. Cheragian et al. performed experiments with nanoparticles such as titanium oxide (TiO$_2$) and silica particles. He found that TiO$_2$ nanoparticles have the highest recovery factors [45]. Williama et al [46] compared copper oxide (CuO) and zinc oxide (ZnO) nanofluids in xanthan gum in waterbased drilling fluids. The nanofluids were prepared with base nanoparticle concentrations of 0.1, 0.3 and 0.5 wt.%. The prepared nanofluids were added as a 1% (by volume) additive to the based drilling mud (WBM). The enhancement in the thermal and electrical properties in the nano waterbased drilling mud (NWBM) was then studied. It was observed that the thermal properties were highly improved by the CuO based NWBM and were more resistant to HPHT conditions compared to the ZnO based NWBM. It was also observed that the nanoparticles played a significant role in stabilizing the viscosity at high temperature [46]. Other widely used nanoparticles include carbon nanostructures and grapheme. These nanostructures generally help improve the rheological properties of the drilling mud at high temperature, increase the stability of the drilling mud, improve the mud sustainability, heat transfer coefficient, and electrical properties of the mud and its dielectric constant, and reduce the fluid loss, corrosion of the drilling equipment, and the torque and drag [47–49]. The effect of different nanoparticles on the rheological properties was investigated by Ismail et al [50]. Nanoparticles such as copper oxide, aluminum oxide, MWCNT, and TiO$_2$ were studied, and their rheological properties, such as their plastic viscosity, yield point, and gel strength, were observed after the inoculation of the nanoparticles in the drilling mud.

2.4.1.1. Plastic viscosity

Ismail et al [50] has found that the plastic viscosity of a water based drilling fluid is reduced after exposure to 121.1 °C. Figure 5 shows the effect on the plastic viscosity. It was observed that not all the nanoparticles followed the same trend. For copper oxide, the trend decreased as the nanoparticle concentration increased. However, the plastic viscosity of the water based drilling fluids with TiO$_2$, aluminum oxide, and MWCNT were slightly higher than the control sample without nanoparticles.
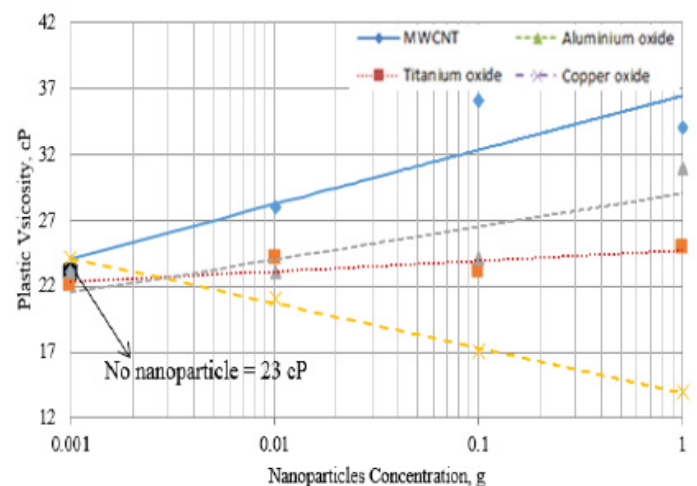

Fig. 5. Effect of the nanoparticle concentration on the plastic viscosity.

Because nanoparticles have a large surface area per volume, their interaction with the matrix andthe surrounding water to based drilling fluid increases. Consequently, they are bond to the base fluid via certain intermediate chemical linkages that improve

the plastic viscosity of the waterbased drilling fluid. According to Ismail et al., the downward trend shown by copper oxide is due to repulsive forces that occur between the copper oxide nanoparticles and the water molecules. This causes the plastic viscosity to decrease with increasing nanoparticle concentration [50].

The rheological behavior may depend on the particle type, size, concentration, and interparticle distance of the nanoparticles in the fluid due to the large surface area of the nanoparticles compared to micron sized and larger particles. According to [50], only approximately 1 lb/gal of nanoparticles is needed to be equivalent to 10 lb/gal of other materials. Reduced solid volumes with increased surface area help maintain the equivalent viscosities of drilling fluids [50, 51]. Paydar and Ahmadi studied the effect of boehmite nanoparticles and xanthan polymers on the plastic viscosity [48]. They observed that a minimum of 1.5 g of xanthan polymers was required to be added to the drilling mud to increase the plastic viscosity (Figure 6), whereas 0.06 g of boehmite nanoparticles was sufficient to cause the same plastic viscosity increase (Figure 7).
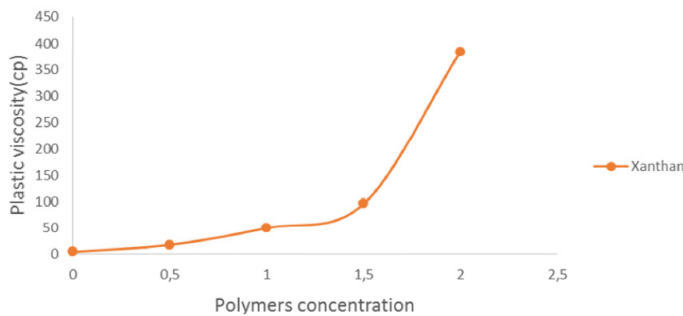
Fig. 6. The effect of different concentrations of xanthan on the drilling mud plastic viscosity [48]
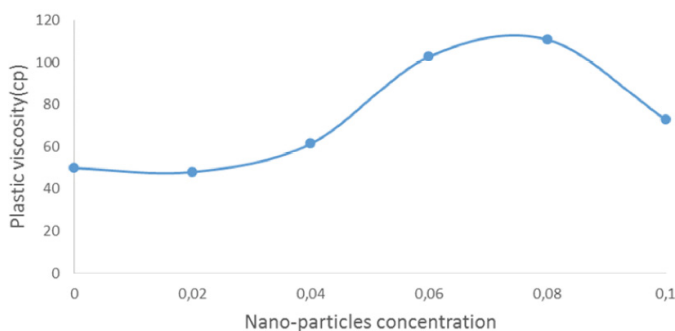
Fig. 7. The effect of different polymer and nano boehmite concentrations on the drilling mud plastic viscosity [48]

They observed that, after 0.06 g of boehmite nanoparticles, the plastic viscosity started to decrease. This was attributed to the fact that, at higher concentration, nanoparticles stick to each other and lose their properties, therefore reducing the efficiency of

the drilling mud and drilling operations. They also concluded that using boehmite nanoparticles in drilling mud is cost effective because it reduces the consumption of polymer materials [48].

2.4.1.2. Yield point

A higher yield point provides a better suspension of the particles in the drilling mud. According to experiments performed by Ismail et al., the yield points of MWCNT and aluminum oxide increase as the nanoparticle concentration increases. However, TiO_2 shows an opposite trend, as shown in Figure 8.
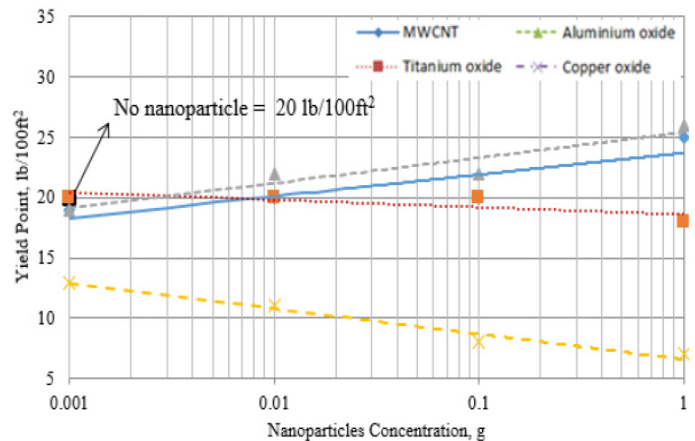
Fig. 8. Effect of the nanoparticle concentration on the yield point.
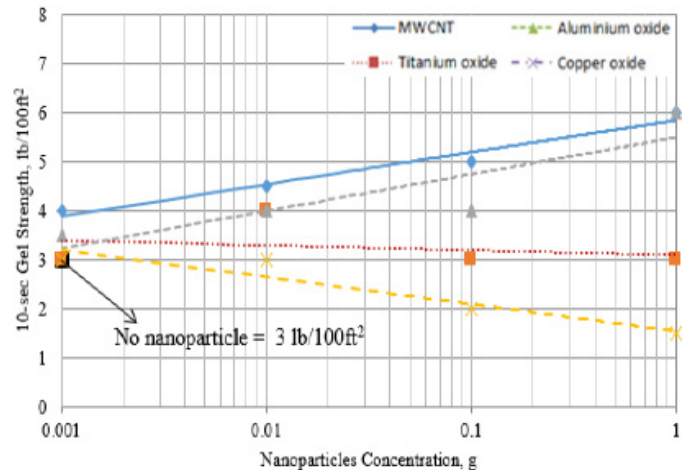
Fig. 9. Effect of the nanoparticle concentration on the 10s gel strength [8].

2.4.1.3. Gel strength

Ismail et al [8] studied the effect of nanoparticles on the gel strength at 10 s and 10 min and found that the gel strength increased for both MWCNT and aluminum oxide with increasing nanoparticle concentration but observed an opposite trend for TiO_2 and copper oxide, as shown in Figures 9 and 10. The electrostatic forces of the nanoparticles cause them

to link with the base fluid within 10 s and 10 min. Due to this interaction, a rigid structure is formed that increases the gelling effect. The decreasing trend for TiO_2 and copper oxide was due to the repulsive forces between the nanoparticles and the base fluid. This caused an expansion between the nanoparticles and the water molecules, reducing the gel strength [8].
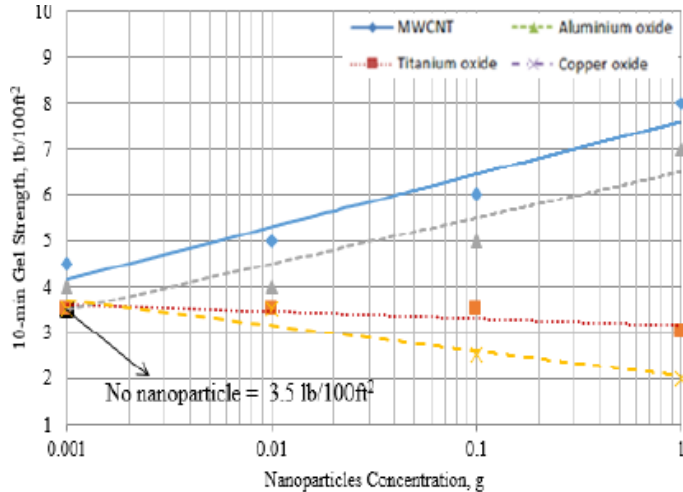

Fig. 10. Effect of the nanoparticle concentration on the 10 min gel strength [8].

2.4.2. Effect of nano based drilling fluids in HPHT environments

The increase in the demand for energy resources, especially petroleum products, has resulted in the depletion of conventional reservoirs. Consequently, today there is a need to explore and extract petroleum from unconventional reservoirs characterized by high pressure and high temperature. The effect of the addition of TiO_2 to drilling fluids was investigated under the HPHT condition. Different concentrations of TiO_2 nanoparticles (0.05 0.1, 0.5 ppb, and 1 ppb) were applied to waterand oil based muds. In WBM, the yield point and plastic viscosity showed an increasing trend with increasing nanoparticle concentration, as shown in Figures 11 to 14. Whereas in synthetic to based mud (SBM), the plastic viscosity increased but the yield point showed a decreasing trend, as shown Figures 15–17. The reason given for this was that the drilling fluid has a thickening behavior under high temperatures. While analyzing the fluid loss experiment using an HPHT filter press, a significant reduction in the fluid loss and a thinner mud cake was obtained. A reduction in the friction coefficient of the water based mud with an average torque reduction of 24 % was reported. In OBM the torque reduction was 23 % [52].
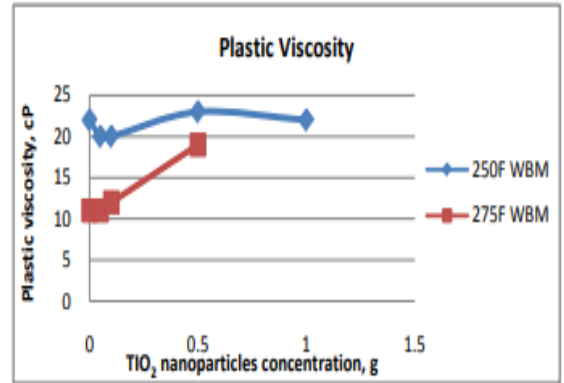

Fig. 11. Effect of TiO_2 nanoparticles on the plastic viscosity of WBM.
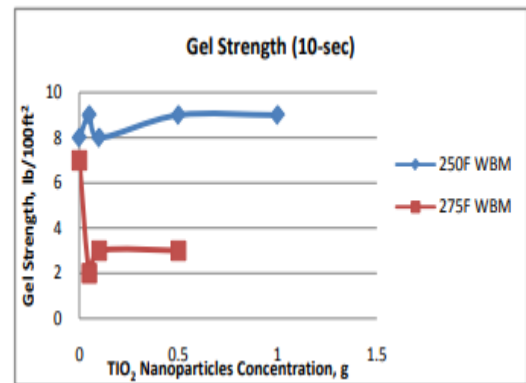

Fig. 12. Effect of TiO_2 nanoparticles on the 10 s gel strength of WBM.
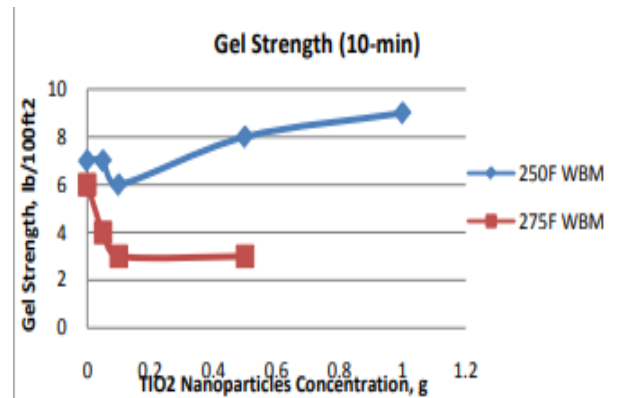

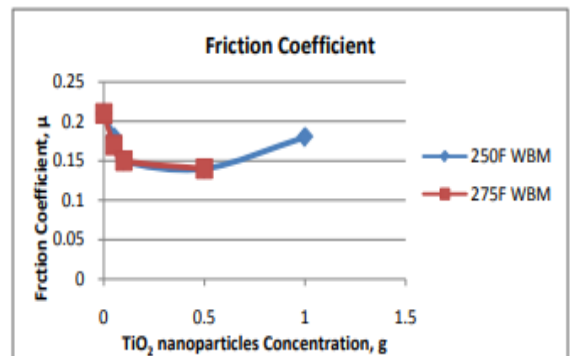Fig. 13. Effect of TiO_2 nanoparticles on the 10 min gel strength of WBM.

Fig. 14. Effect of TiO_2 nanoparticles on the friction coefficient of WBM.
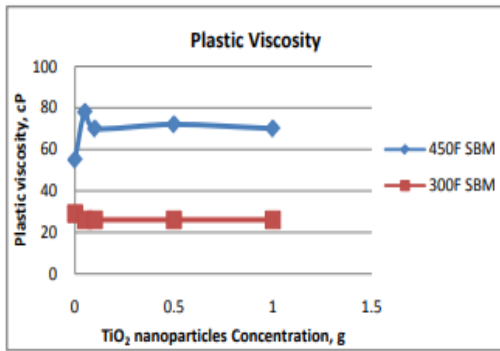
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Fig. 15. Effect of TiO$_2$ nanoparticles on the plastic viscosity of SBM [52]
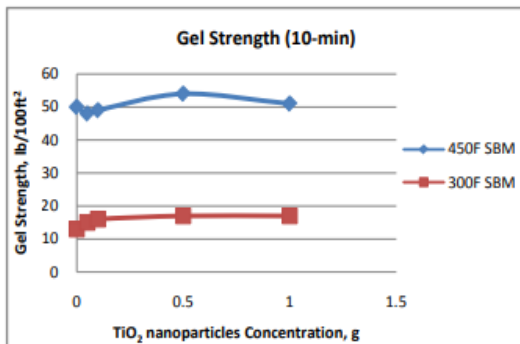

Fig. 16. Effect of TiO$_2$ nanoparticles on the 10 min gel strength of SBM [52].
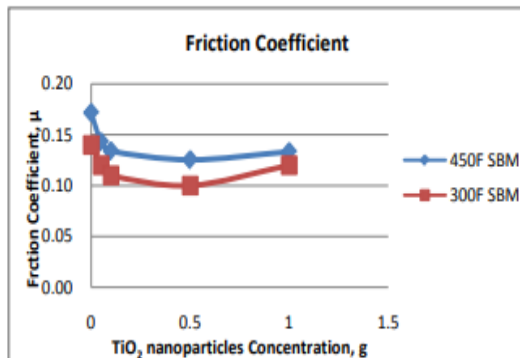

Fig. 17. Effect of TiO$_2$ nanoparticles on the friction coefficient of SBM [52].

Drilling operations at HPHT conditions is challenging as the performance of conventional additives becomes limited as they starts degrading. Drilling HPHT wells, in environments above 150 °C and 690 bar, is very difficult due to deep water operation as wells drilling deviated wells [53, 8]. Using conventional micro and macro based drilling fluids in such extreme conditions is difficult due to their low thermal stability. The thermal degradation of such fluids starts above 125 to 130 °C; therefore, they cannot perform effectively in the mud system. Nanoparticles having high thermal conductivity with a high

tolerance to high pressures and temperatures have been found to be effective in HPHT environments [53]. In addition, it has been observed that the viscosity of drilling fluids decreases with increasing temperature. This limits the capability of drilling fluids to drill deep. Nanomaterials of different types, sizes, and compositions can provide drilling fluids with definite viscosities that are thermally stable [54]. The oil industry views this as an opportunity to develop a cost-effective and environmentally sustainable drilling fluids that fulfill the necessary technical requirements.

2.4.3. Reduction in the loss circulation

Lost circulation is the uncontrolled flow of drilling mud into a formation. This leads to various consequences such as an increased time required to reach the drilling target depth, a loss of pressure control, increases in safety concerns for the rigs, and the contamination of water leads [55]. The performances of the multiple loss circulation materials that are currently available in micro and macro sizes are not adequate. The addition of these loss circulation materials continuously increases the weight of the mud, decreasing the ability of the drilling fluids to carry cuttings to the surface.

The application of nanoparticles could lead to a reduction in the loss circulation by imparting a sufficient carrying capacity to transport and drop off the cuttings efficiently while maintaining its density and pressure over a wide range of operational conditions [55–57]. This would save a huge amount of revenue, especially in the case of oil-based muds. The reduction in the fluid loss with the addition of nanoparticles and its efficiency is compared to that of regular additives in Figure 18.
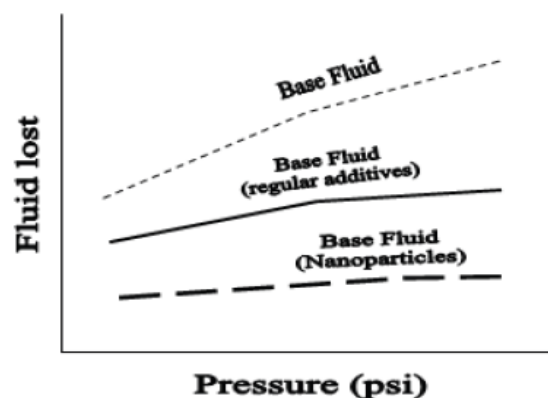

Fig. 18. Reduction in the fluid loss with increasing pressure [54]

2.4.4. Reduction in the erosion of the borehole

Erosion of the borehole primarily occurs when the fluid comes into contact with obstructions. Obstructions cause the fluid to experience a swirling effect that starts to erode the sides of the borehole. To minimize this erosion, the viscosity and velocity of the fluid must be optimized. A comparison of a regular base fluid (without additives), a base fluid with regular additives, and a base fluid with nanoparticles instead of regular additives shows an improvement in the drilling fluid performance with nanoparticles (Figure 19) [54]. The erosion of nano-enhanced drilling mud is much less than the erosion of the drilling mud with no nanoparticles and that of mud with regular additives. The erosion tends to decrease as the velocity decreases with increasing viscosity.
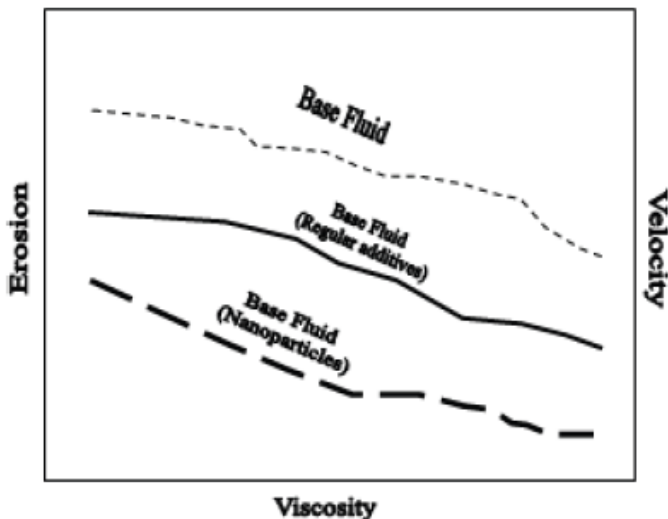

Fig. 19. Reduction in the velocity and erosion with increasing viscosity [54].

2.4.5. Increase in the wellbore stability

Nanoparticles have the potential to increase the wellbore stability. Achieving shale stability is a complicated problem, especially when using WBM. In such situations, using a specially designed nanoparticle in water-based mud can play an important role in achieving wellbore stability. Ultrafine nanoparticles are much smaller than the pore throat sizes of shales. Consequently, they efficiently plug the pore spaces. Shale nano-scaled pores warrant the use of nanoparticles as mud additives to plug pores by forming filter cake internally and at the wellbore wall [58].

2.4.6 Reduction in the torque and drag

While drilling horizontal and extended reach wells, a dramatic increase in torque and drag problems are observed. Consequently, there is continuous friction between the casing drill string and the borehole wall, resulting in damage and a reduction in the thermal stability. Nanoparticles have a very fine and thin film formation capability unlike traditional micro- and macro-material-based drilling muds, which have limited capabilities. The frictional resistance between the pipe and the borehole wall can be significantly reduced due to the formation of a thin lubricating film on the wall–pipe interface [55].

According to Abdo et al [54], as the load increases the friction coefficient also increases. This increase can be reduced using nanoparticles. The friction between the drill string and the borehole increases persistently with an increasing load. The performance in such a system is shown in Figure 20.
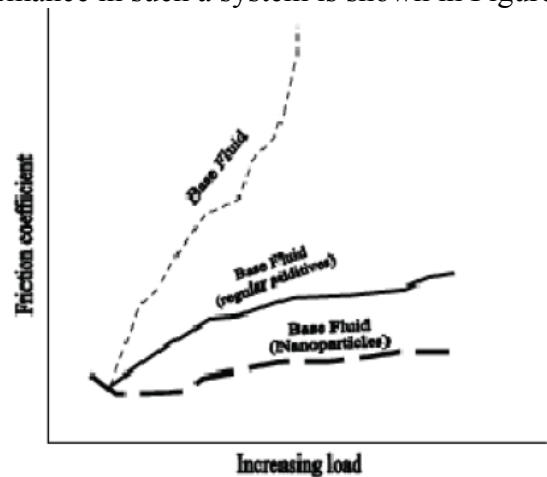
Fig. 20. Reduction in the friction coefficient with increasing load.

According to Bialy et al., the torque and drag can be reduced by using spherical particles in drilling fluids [7]. They experimentally observed that using manganese tetraxide with a particle size of 50 μm and formulating it with potassium formate drilling fluids improves the equivalent circulating density and plastic viscosity [59, 60].

Hydrophobic nanoparticles of silicon dioxide (SiO_2) also reduce the drag when they are injected into micro-channel reservoirs because they get adsorbed on the wall, forming a super hydrophobic layer that restricts the flow resistance [60, 61].

2.4.7. Reduction in pipe stuck problems

Mechanical and differential pipe sticking is a common problem encountered while drilling. Ultrafine mud cake is formed by nano-drilling fluids on the surfaces of formations, and a non-sticking film develops on the downhole tools.

2.4.8. Reduction in bit balling

Bit balling is a severe problem generally encountered while drilling reactive formations such as gumbo shale. A drastic reduction in the rate of penetration (ROP) is observed as clay accumulates in the tooth gap of the bit [53]. Nano-based fluids form a hydrophobic film that acts as a barrier to bit balling [53].

2.4.9. Improvement in the rate of penetration

A reduction in the above-discussed problems will ultimately improve the ROP and save on the enormous cost of drilling operations. The non-productive time can also be reduced significantly because nano-drilling fluids allow the target depth to be reached in a shorter period of time. Abdo et al made a tentative performance comparison of the ROP for different base fluids [54], as shown in Figure 21. From the figure, it is clear that nano-enhanced drilling mud can drill deeper in less time.
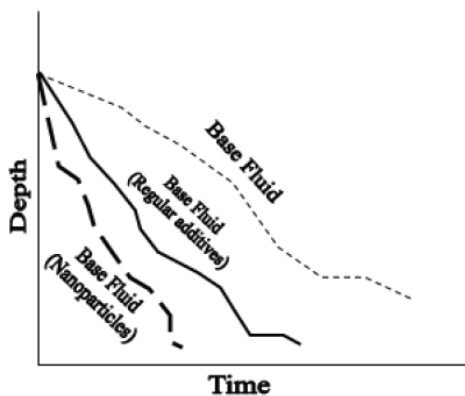

Fig. 21. Improvement in the rate of penetration (ROP) [54].

2.4.10. Cement property enhancement

During drilling and completion operations, one of the most important processes in drilling is cementing. Despite the use of smart polymeric additives, fibers, and self-healing materials, achieving long-term zonal isolation is very challenging [73]. Without complete zonal isolation, a well will never reach its full production potential. The economic longevity of an oil and gas producing well is directly linked to the quality of the cementing job [63]. The performance of conventional cement-based materials in bottom-hole conditions is very poor because these materials possess low tensile strength, experience bulk shrinkage, and are naturally brittle. This ultimately leads to a reduction in the production capacity, an increase in repair costs and environmental issues, and, in the worst case, the loss of the well [62, 64]. To deal with the various stressful conditions over the entire life of a well, the conventional cement system can be converted into a multifunctional, durable system via the application of nanotechnology [64]. Thermal and stress conditions, which are introduced due to hydraulic fracturing, production, completion, steam injection, or remedial treatments during the life of a well, also pose a significant challenge to the cement sheath integrity [65]. A nanoemulsion technology based on nanospacers has been introduced to enhance the mud displacement efficiency, resulting in better mud removal, wettability changes, and better casing/formation adhesion of the cement sheath [66]. Nanomaterials have been applied in the oil well cementing industry to accelerate cement hydration [67], improve the mechanical properties of the cement sheath [68], reduce the probability of casing collapse, and prevent gas migration [69].

2.4.10.1. Requirements for long-term zonal isolation

The ability of a cement system to provide zonal isolation for a longer period of time depends on factors such as the mechanical properties of the cement sheath, the formation, the geometry of the cased wellbore, and the well condition [70]. Factors such as the volumetric instability and the imposed tensile stresses beyond the tensile strength of the cement sheath contribute greatly toward the failure of cement sheaths.

2.4.10.2. Improvement in the tensile properties

A flexible cement system exhibiting a high tensile strength to Young modulus with high resistance to fatigue and low shrinkage is a primary requirement for long-term zonal isolation. Nanoscale fibers have attracted research attention in the last several years [71-74]. Carbon nanotubes (CNTs) and nano-fibers (CNFs) have extremely high strength with Young moduli on the order of several terapascals and tensile strengths in the gigapascal range [75]. Several experimental studies on the impact of CNTs

and CNFs on cement-based material properties are shown in Table 2 [62, 70, 76–78]. It has been observed that the addition of 0.1 % MWCNTs to an oil well cement paste without surfactants reduces the tensile strength by approximately 30 % [78]; while well-dispersed CNTs resulted in a significant increase in the flexural strength, stiffness, and deformation ability [72, 76, 77]. An approximately 260 % increase in the tensile strength was observed when adding 0.2 % MWCNTs [76].

Table 2. Experimental studies on the impact of CNTs and CNFs on cement-based material properties [70].

Fiber	Content (wt. %)	Size		w/c*	Curing time (d)	Flexural strength (MPa)	E (GPa)	σ_t (MPa)	$\sigma_t/\sigma_{t,Ref}$	E/E_{Ref}	Ref.
		Diameter (nm)	Length (μm)								
Short-MWCNT	0	20–40	10–30	0.3	28	9.3	16.4	3.1	1.00	1.00	(Konsta-Gdoutos et al., 2010)
	0.048					10.8	-	3.5	1.13	-	
	0.08					12.7	21.9	4.2	1.35	1.34	
	0.1					11.5	-	3.8	1.23	-	
Short-MWCNT	0	9.5	1.5	0.4	28	3.3	14.5	0.6	-	-	(Abu Al-Rub et al., 2012)
	0.04					3.8	12.2	0.7	1.17	0.84	
	0.1					4.5	15.2	0.8	1.33	1.05	
	0.2					11.9	17	2.2	3.67	1.17	
Long-MWCNT	0	20–40	10–100	0.3	28	9.3	16.4	3.1	1.00	1.00	(Konsta-Gdoutos et al., 2010)
	0.025					11.5	21.9	3.8	1.23	1.34	
	0.048					11.5	20.2	3.8	1.23	1.23	
	0.08					10.2	-	3.3	1.06	–	
Long-MWCNT	0	< 8	10–30	0.4	28	3.3	14.5	0.6	1.00	1.00	(Abu Al-Rub et al., 2012)
	0.04					5	15.2	0.9	1.5	1.05	
	0.1					5.3	13.0	1.0	1.67	0.90	
CNF	0	60–150	30–100	0.5	28	5.5	8.8	1.8	1.00	1.00	(Metaxa et al., 2010)
	0.048					7.2	13.2	2.4	1.33	1.5	
MWCNT	0	13–18	3–30	0.54	7	-	7.2	2.6	1.00	1.00	(Santra et al., 2012)
	0.1					-	7.1	1.8	0.69	0.99	
	0.2					-	7.2	2.5	0.96	1.00	

* Water-to-cement mass ratio

Nanoparticles having a very high surface area-to-volume ratio can act as nuclei for cement hydrates, promoting cement hydration [67, 79]. Nanoparticles, when mixed with a cement slurry, produce a viscous slurry, which might lead to an impairment in the homogeneous dispersion of nanoparticles in the slurry [80]. The potential properties of nanocomposites can only be achieved via the effective dispersion of nanoparticles in the matrix [81]. Experiments have shown that the addition of 5 and 3 % nano-SiO_2 and 5 % TiO_2 decreases the flexural strength of the concrete. This decrease has been attributed to weak zones caused by the agglomeration of nanoparticles [72, 82]. The impact of various metal oxide nanoparticles on the tensile strength has also been studied. It was observed that a system containing 4 % nano-SiO_2 showed a significant tensile strength enhancement. TiO_2 and zinc peroxide nanoparticles also showed similar trends. In addition, it was observed that increasing the concentration beyond 4 % led to a reduction in the tensile strength [85–87]. For aluminum oxide and chromium oxide, the optimum concentration was 1 % [83–87]. Nanoscale particles improve both the flexibility and the tensile strength. Therefore, zonal isolation is possible even under high stress conditions [62]. Even though thermoplastics such as polyamide, polypropylene and polyethylene, styrene divinylbenzene, or styrene butadiene provide great flexibility in cement systems, their performances decrease sharply when exposed to high temperatures because they either melt or deteriorate at high temperatures. Even though some thermoplastics are stable at high temperatures and in highly alkaline environments, their high costs limit their usage [88]. It has been observed that nano-rubber particles produce an impressive toughening effect [89]. When nanoscale powdered rubber particles are introduced into epoxy resin, the tensile strength either increases or remains unchanged [85, 90].

2.4.10.3. Reduction of shrinkage

The self-inflicted bulk shrinkage of cement-based materials is called autogenous shrinkage. The reac-

tion between water and cement is associated with a reduction in the volume because the reaction products fill less space than the reactants. This is called chemical shrinkage and is a fundamental property of cement hydration [91]. Nanoclay can serve as an internal water reservoir. The water-retaining capacity of nanoclay can be used to provide extra water for further hydration [92]. It was observed that the addition of 1.5 and 3 wt.% clay nanoparticles to cement mortar reduces the autogenous shrinkage by 43 and 40 %, respectively. However, a system that contained 4.5 wt. % nanoclay showed a 1.5 % increase in shrinkage compared to the control system [93]. Nano-magnesium oxide (MgO) resulted in a major reduction in the autogenous shrinkage compared to nano-calcium oxide (CaO), mostly because the nano-CaO reacted very quickly and the main reaction occurred prior to the initial setting. Nano-MgO reacts slower than nano-CaO and can more effectively compensate for long-term shrinkage. In addition, at elevated temperatures and when pumping the cement slurry to great depths in oil wells, nano-MgO is more efficient [94].

3. Advantages of Nanotechnology in the Oil and Gas Industries

The high water production of wells is a severe problem faced by the oil and gas industries. Polymers such as polyacrylamide are generally used to reduce the water production. However, polymers are not always effective for all types of formations, especially shale formations. This is due to the size of the polymers, which makes them unable to plug the pore spaces of the formation. Under such conditions, nanoparticles can play a crucial role. Nanomaterials can easily plug the pore spaces in water or gas producing zones due to their smaller size and increased surface area. This in turn increases the surface free energy and associated structural perturbations [95, 96].

Polymer-coated nanoparticles have been used to improve the mobility control and alter the wettability [97]. The sizes of nano-polymer microspheres can be adjusted according to the pore throat size of the formation. Because the microspheres are elastic, they can deform and move forward under certain pressures. They can resist high temperatures up to 110 °C and high salinities up to 200,000 mg/L [95]. This polymer microsphere technology has become an effective method for profile control and water plugging in seriously heterogeneous and high-

temperature reservoirs [97]. According to Tongwa and Bai, the swelling performance, post-degraded gel viscosity, and long-term thermal resistance of a nanocomposite gel can be increased by several orders of magnitude compared to hydrogels with no nanomaterials [98]. Patil and Deshpande developed an environmentally acceptable conformance sealant that incorporates nanosilica and an activator [99]. This system can effectively prevent water and gas flow at temperatures up to 300°F148.8°C. An increase in the pH to more than 7 leads to the surface ionization of silica particles, which exhibit charge repulsion and ultimately result in an increased gelation time. The nanoparticles can plug the pores and microfractures in shale, preventing water invasion.

Silica nanoparticles have proven to be very effective sealing agents. Such nanoparticles have been used to control water invasion in the Kazhdumi shale in southwestern Iran. Kazhdumi shale has a very low membrane efficiency of approximately 1.8 % and is highly prone to water invasion. Consequently, this shale is highly unstable. Moslemizadeh and Shadizadeh studied the effect of silica nanoparticles on fluid invasion in this shale by increasing the concentration of nanoparticles from 2 wt. % up to 10 wt.% [100]. They observed that the fluid invasion into the shale decreased as the size of the nanoparticles increased from 10 nm to 25 nm. However, even though the invasion decreased, the plugging time of the pores in the shale by the nanoparticles decreased from 17 h to 11 h. The fluid invasion reduction efficiency with the highest weight percent of 25-nm nanoparticles was found to be 72.76 % compared to 52.93 % for the 10-nm nanoparticles, as shown in Figure 22.
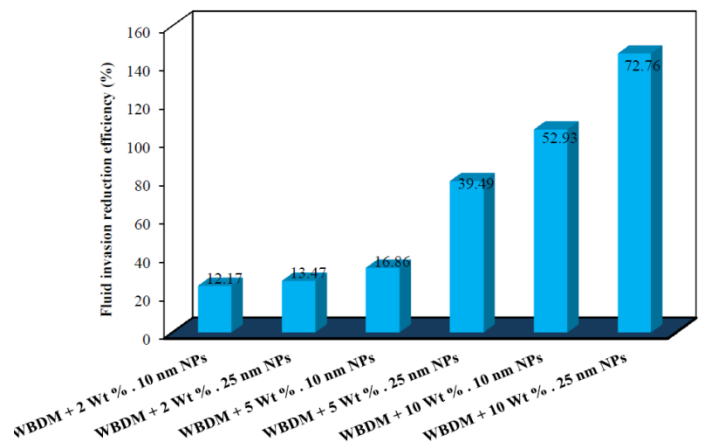

Fig. 22. The effect of the size and concentration of nanoparticles on the fluid invasion reduction efficiency [100].

4. Waste Management in Oil Industries

Wastewater produced in oil industries can be treated using nanofiltration methods. Nanofiltration is a membrane separation technology that functions using reverse osmosis and ultrafiltration. Water injected during secondary and tertiary recovery can be purified and desalinated using this technology. A nanomembrane separates the wastewater of the produced liquid into an oil-rich water phase and an oil-free low salinity water phase. The oil-rich water phase is converted via demulsification and dehydration, and the oil-free low salinity water phase is prepared directly for reinjection [101-103]. Substances such as polymers, surfactants, and alkalis present in the produced liquid can also be separated, reducing the cost of enhanced oil recovery.

Nanoparticles can be used as a photocatalytic agent because they have the ability to undergo redox reactions under ultraviolet radiation. This helps in purifying contaminants, organic matter, and oilfield sewage [104]. Photocatalytic reactions with TiO_2 occur only after it is excited by ultraviolet light [105]. By means of ion doping, semi-conductor compound, surface photosensitive catalytic degradation and TiO_2 surface amorphization ,catalytic efficiency of visible light can be increased. Efficiency of the ultra violet rays can be increased by these methods which will make the nanoparticles more effective for purification process.Graphene-like carbon nitride is capable of photocatalytic water decomposition. Problems with catalytic agent separation and recovery by means of TiO_2 immobilization, micrometer/nanometer structures, and magnetic substance immobilization can be solved [106]. TiO_2 photocatalytic technology can be applied in oil fields to remove trace organic matter in water.

5. Environmental Aspects of Nanoparticles in the Oil and Gas Industries

Nanotechnology can make the petroleum industry considerably greener. Pollution from these industries today is an important aspect that is gaining worldwide importance. Hydrogen sulfide is a highly corrosive and toxic gas that can permeate into permeable formations during drilling operations. It is very important to remove this gas from the mud not only to protect the health of workers but also to reduce environmental pollution and prevent the corrosion of pipelines and drilling equipment. According to Sayyadnejad et al., zinc oxide particles with sizes of 14–25 nm and specific surface areas of 44–56 m^2/g can completely remove hydrogen sulfide from water-based drilling fluid whereas only 2.5 % of the hydrogen sulfide could be removed by bulk zinc oxide, which was also found to be time consuming [107]. For elemental mercury removal from vapors such as those coming from combustion sources, silica–titania nanocomposites can be used. Silica enhances adsorption, and titanium photocatalytically oxidizes the elemental mercury to less volatile mercuric oxide [108].

6. Conclusions

The application of nanotechnology in oil exploration and production has been proven capable of reaping great benefits. In every aspect of oil exploration and production, nanoparticles have shown positive results. They have been a boon in the field of enhanced oil recovery due to their ability to alter the wettability of reservoirs. They are a promising solution for exploring and extracting crude oil out of HPHT reservoirs. While most additives used to encounter such HPHT situations, such as polymers, start degrading after some time, nanoparticles have shown the potential to bear such environments because they are highly thermally stable compared to other additives. The main reason for this is their high surface area-to-volume ratio, which makes the heat transfer process very efficient. When nanoparticles are used as an additive in drilling fluids, a smart nanofluid that has shown appreciable benefits compared to conventional drilling fluids used today in oil industries is formed. The ultimate goal of drilling mud is to reduce the cost of drilling by reducing consumption and improving the properties of the drilling mud. The various technical and environmental problems encountered while drilling can easily be reduced by using nanomaterials. Nano-enhanced drilling mud will not only increase the longevity of the downhole equipment but also provide a qualitative fluid for interactions with HPHT formations. Nano-based fluids provide a better replacement than conventional drilling muds. According to an extensive literature survey, approximately 1 lb (0.453kgs) of nanoparticles can replace 10 lb(4.535 kgs) of conventional additives used in drilling mud. Therefore, the high cost of additives can be reduced. Nanoparticles have the potential to become a permanent constituent of drilling mud because they can overcome many downhole problems. Nano-based drilling mud will therefore pave a way to reach hydrocarbons that are not easily accessible.

Nomenclature

IFT – Interfacial Tension
ROP – Rate of Penetration
WBM – Water-based Mud
OBM – Oil-based Mud
NWBM – Nano-water-based Mud
MWCNTs – Microwalled Carbon Nanotubes

CNTs – Carbon Nanotubes
CNFs – Carbon Nanofluids
MgO – Magnesium Oxide
CaO – Calcium Oxide
TiO_2 – Titanium dioxide
SiO_2 – Silicon dioxide
HPHT – High Pressure High Temperature

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