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Application of Nanotechnology for Enhancing Oil Recovery (EOR) in Oil and Gas Industry: A Review

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Abstract: *This paper presents a review on the application of nanotechnology for enhancing oil recovery in oil and gas industry. Different types of nanoparticles; metallic, metal oxide, inorganic organic and magnetic nanoparticles has been reviewed. Application of nanotechnology in oil and gas industry has been revised in enhanced oil recovery, corrosion and scale inhibition, drilling and hydraulic fracturing fluids, exploration and reservoir characterization, reservoir cementing, production and stimulation. Challenges and current research gaps; cost ineffective route for synthesis and delivery of nanoparticle, mechanism for migration and transport behaviour of nanomaterials through a porous media, determination of size of nanomaterials to secure effective penetration into porous reservoir and agglomeration of nanoparticles in a coarse and harsh conditions of sub-surfaces were also discussed.*

Key words: *Nanotechnology, Nanoparticle, Oil and Gas, Enhanced Oil Recovery, Heavy Oil Recovery*

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I. Introduction

In oil and gas industry, it is projected that in about 30 years' time, the global energy demand must have risen as high as 60%. This challenge can only be met through energy science revolutionary breakthrough and advanced technologies (Campelo*et al.,* 2009). Oil and gas industries has been in search of a striking technological discovery in the underlying core science and engineering. The current insight in nanotechnology has opened up the possibilities of going beyond the energy supply alternatives through the introduction of technologies that are environmentally friendly and super-efficient. Nanotechnology is characterized by the use of materials in designs and production at the nanometer (nm) scale. Its design is in collaboration among several disciplines which makes it inseparably innovative and very concise compared to other technologies. Nanotechnology has been projected to be the groundwork and cornerstone of any future energy technology, which could offer the greatest possibility for innovative solutions (Subbiah*et al*., 2010 and Serrano *et al*., 2009).

Nanotechnology involves the use of nanoparticles, nanotubes, nanofluids/smart fluid, nanoemulsion and nanocatalyst which is in the range of 1-100nm (Fakoya*et al.,* 2018) for wettability alterations, mobility control, enhancing steam injection, well completion, modification of interfacial parameters by nanostructured surfactants in enhanced oil recovery process, enhancing abrasion and corrosion resistant by nanostructured coatings, improvement in precision and sensitivity in sensors during exploration, strengthening and increasing durability in oil well cements, separation by nanostructured membranes during oil production, adsorption by nanoparticles in asphathene removal, nanoparticles for scale inhibition during scale formation control and in well completion through nanocoatings. It also involves the synthesis and utilization of nanoparticles, nanotubes, nanofilms and nanofibers (Xu *et al.,* 2015).

The application and advanced study of these small materials between 1-100nm is currently one the fastest growing research area in in engineering and science at large because of they are ecosystem friendly. The innovation and Nano-technological development has led researchers to fabricate collection of different unique and enhanced nanodevices, nanotools and nanomaterials which can be used in various areas including electronics, medicals, biomedical, aerospace, photography, energy, smart materials, manufacturing and pharmaceutical (Alshehri*et al*., 2012; Shen *et al.,* 2014; Kumar *et al*., 2015; Xu *et al*., 2015; Subbiah*et al*., 2010; Serrano *et al*., 2009; Mout*et al*., 2012; You *et al.,* 2013; De Jong and Borm, 2008 and Otsuka *et al*., 2003). This is because their physical and chemical properties are size-dependent which are not often observable in their bulk counterparts (Kim *et al.,*2014). The number of atoms at the surface of a bulk material is always smaller than the number of atoms in the bulk.

Therefore, their physical and chemical properties are mostly constant regardless of their sizes.

The reduction of the size of a particle to a wavelength less or near its electron conduction, many properties and features such as optical behaviour, magnetism, thermal resistance, melting point, internal pressure, chemical and catalytic activities are altered. This is due to the surface to volume ratio which exponentially becomes larger and the number of atoms on the surface also becomes appreciable with regards to the amount of atoms in the bulk solution (Saidur*et al*., 2011). This idea has allowed researchers to utilize these unique properties for many different applications. Also, nanotechnology is a cost-effective, cost-efficient industrial process and offers a precise design and manipulation of atoms and molecules as well the as full control on their unique properties (Serrano *et al*., 2009).

However, the high global demand for energy and the remaining major challenges in the application of current conventional procedures have forced researchers to embark on the search for more economical, efficient and environmentally sound techniques to extract more hydrocarbons. In refinery processes, the drilling platforms and equipment are made so as to resist corrosion towards water and air, resist shock and wear, enhanced durability and thermal conductivity. This is carried out by coating them with different nanoparticles (Saidur*et al*., 2011).

Different types of nanoparticles exist in nanotechnology, these are generally classified as quantum dots, graphene, carbon nanotubes, fullerene, polymeric particles, metal oxides and metallic (Kapusta*et al.*, 2011). Generally, there are four types of nanoparticles; (a)Organic nanoparticle (b)Metallic and metal oxides nanoparticles (c)Inorganic nanoparticle (d)Magnetic nanoparticles (Negin*et al.*, 2016; Khalil *et al*., 2017).

1.1 Metallic nanoparticles

Metallic nanoparticles consist of alkali metal, alkaline metal earth, transition metals, lanthanides, and actinides (Fakoya*et al.*, 2018). They are generally more expensive than the non-metallic nanoparticles. Due to the unique chemical and physical characteristics of metallic nanoparticles, several metallic nanoparticles have been used in wide variety of oil and gas applications, from exploration to production. In most cases, both noble and transitional metal nanoparticles are mainly used as catalyst in many petroleum-related processes such as catalytic reforming, hydro-reforming, hydro-denitogenation, in-situ aquathermolysis, hydrocracking and hydro-desulphurization (Khalil *et al.*, 2015 and Maity*et al.*, 2010). However, this is mainly as a result of large surface area-to-volume ratio of these metallic nanoparticles in comparison to their bulk counterparts, which significantly improves their catalytic activities and selectivities (Campelo*et al.*, 2009).

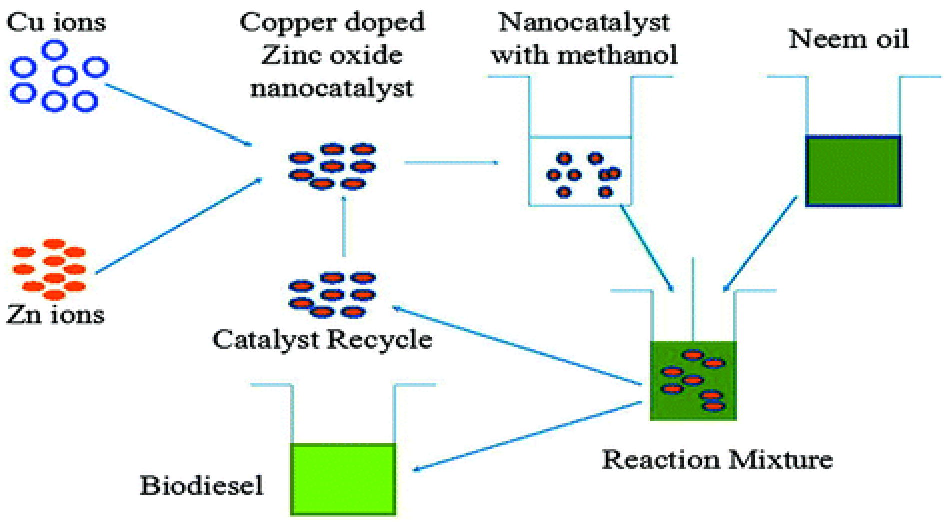

Fig. 1: Functions of metal oxides in nanoparticle synthesis

Generally, there are four most common methods through which metallic nanoparticle can be synthesized;

a. Reduction of metal salt precursors
b. Reduction of organic ligands in organometallic precursors
c. Metal vapour chemistry
d. Electrochemical synthesis (Pachón and Rothenberg, 2008; Kapusta*et al.*, 2011).

1.2 Reduction of metal salts precursors for synthesis of metallic nanoparticles

Reduction of metal salt precursors is the most commonly used and simplest method for manufacturing of metallic nanoparticles. Research showed that several nanoparticles have been synthesized through this fabrication process. The metal oxide nanoparticles are manufactured using liquid to solid and gas to solid phase fabrication process. Silver, Copper, Osmium, Palladium, Platinum, Gold, Iridium and Rhodium metallic nanoparticles have been synthesized using reduction of each metal salt precursor in the presence of a stabilizing agents to prevent particle aggregation (Ayyapan*et al.*, 1997; Jana *et al.*, 2001; Sanyal and Jagirdar, 2012 and Wostek-Wokciechowska*et al.*, 2005). The general scheme for this fabrication process is represented in figure 2(Khalil *et al.*, 2017; Pachón and Rothenberg, 2008).

Generally, the metal cation contained in the solution with the help of a reducing agents such as hydrazine, carbon monoxide, hydrogen and hydrides are reduced to metal atoms. The formation of the nanoparticle is a stepwise reaction process which involves nucleation, growth and agglomeration (Murphy *et al.*, 2005; Roucoux*et al.*, 2002 and Rodríguez-León *et al.*, 2013). The rapid clustering of the metallic atoms leads to the formation of nuclei of metallic nanoparticle which are also referred to as seed particles. The seed particles grow together to form very stable and larger metallic nanoparticles as a by-product. The addition of stabilizing agents such as surfactants, organic ligands and polymers at this stage controls the growth and aggregation of the particle, this also controls the shape and morphology of the nanoparticles formed (Pachón*et al.*, 2008).

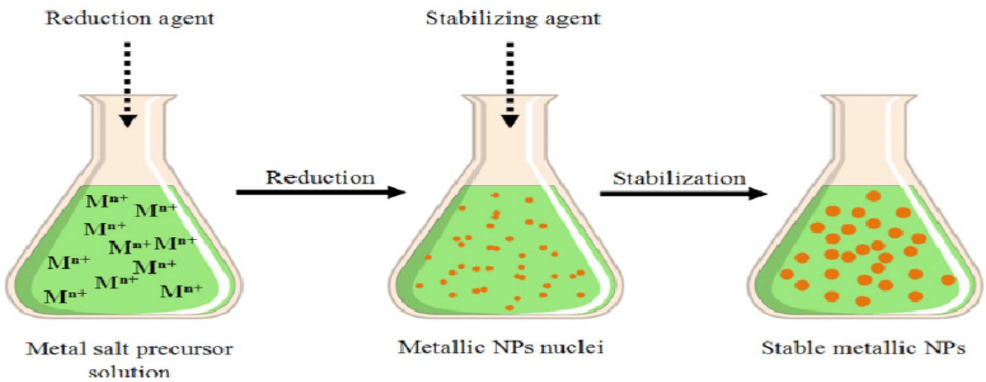

Fig. 2; Metal salt reduction process-the most commonly used technique for fabricating metallic nanoparticles (Khalil *et al.*, 2017) from (Fakoya*et al.*, 2018).

The stabilizing agent has the ability to change the surface energy of particles and alter the growth and aggregation level at the metal surface. Through this process, nanoparticles having different properties in different directions; thus non-isotropic such as nanocube, nanowires, nanoplates, and nanorods can be synthesized depending on the type and amount of stabilizing agent (Yang *et al.,* 2010; Lofton and Sigmund, 2005 and Huang *et al.*, 2011).

1.3 Reduction of organic ligands in organometallic precursors

This is one of the processes for synthesis of metallic nanoparticles through the reduction of organic ligands contained in an organometallic precursor. In this process, the precursor of organometallic compound is used as the metal other than using a metal case as in reduction of metal salt precursor for synthesis of nanoparticles. Organometallic precursor helps to prevent the inactivity of excess water and salt on the surface of the particles during the particle growth and aggregation which can change the metal precursor's reactivity by producing oxides or hydroxides with a very thin layer (Philippot and Chaudret, 2003). Different metallic nanoparticles have been reportedly synthesized from different organometallic precursors (Philippot and Chaudret, 2003; Chaudret, 2005).

The approach of organometallic has been dated long 15 years, having its benefit from the metal complex reactivity towards ligand displacement or reduction of ligands (Philippot*et al.*, 2003; Chaudret, 2005). In this approach, reactions are likely to take place in very mild conditions (usually below or at room temperature) and a rigorous control of the surface species may be achieved. The main precursor is an organometallic complex with an olefinic or polyolefinic ligand which are able either to be hydrogenated to give a bare metal atom that would condense in the reaction medium or to be substituted by CO to give an unstable intermediate. Prototypes of such complexes are $Ru(C_8H_{10})(C_8H_{12})$ and $Ni(C_8H_{12})_2$ which can satisfactorily decompose under dihydrogen in a mild condition. Complexes which can accommodate alkyl, allylic or cyclopentadienyl groups may also decompose easily, for example $Co(C_8H_{13})(C_8H_{12})$, $Rh(C_3H_5)_3$ and $PtMe_2(C_8H_{12})$. At difficult situations, when olefinic precursors are not readily available, more complex structures can also be used. For example, M(dba)2 (dba = dibenzylidene acetone; M = Pd; Pt) is a good precursor for the preparation of nanoparticles of Pd or Pt after treatment with dihydrogen or carbon monoxide (Philippot and Chaudret, 2003; Chaudret, 2005).

1.4 Metal vapour chemistry

Metallic nanoparticles can also be synthesized by a method called metal vapour chemistry also referred to as chemical vapour synthesis. This involved the use of various materials such as chlorides, organometallics, hydrides, volatile compounds and carbonyls as precursors for the production of their corresponding metallic nanoparticles. A review on the practical procedure for metal vapour chemistry, its synthesis and current advancement has already been reported (Swihart, 2003). Metal vapour chemistry or chemical vapour synthesis is initiated through a rapid evaporation of the metal precursors which causes the formation of atomic vapour of the metal involved. This metal vapour is further condensed into a very cold liquid with a stabilizing agent that would initiate the formation of the corresponding metallic nanoparticles (Swihart, 2003; Pachón*et al.,* 2008).

1.5 Electrochemical synthesis

This is also one of the methods for the synthesis and fabrication of nanoparticles. It was introduced by Max Planck Institute research group. In electrochemical method, synthesis of nanoparticles is through the process of electrochemical redox reaction between the sacrificial anode containing the bulk metal and the cathode. Electrochemical synthesis of nanoparticles is initiated through the oxidation of the bulk metal contained in the cathode for form metal ions (Reetz and Helbig, 1994; Yang *et al.,* 2010; Kapusta*et al.,* 2011).

The metal ion formed travel to the cathode where the ions are reduced to ad-atoms or zerovalent metal atoms as a seed particle. The seed particles further grow and cause the formation of a very stable metallic nanoparticle. Research showed that different collection of both noble and transitional metals nanoparticles such as Fe, Ag, Pd, Au, Co, Ti, and Ni, as well as other bi-metallic alloy nanoparticles such as Fe-Ni, Pd-Ni, and Fe-Co have been successfully synthesized using electrochemical synthetic process (Reetz and Helbig, 1994; Liu *et al.,* 2013 and Huang *et al.,* 2006).

1.6 General scope from the evolution of nanotechnology in oil and gas industry

The evolution of nanotechnology has cut across many sections of oil and gas industry and currently acting as a technology enhancing a quantum leap in the industry. These sections ranges from every unit operation of petroleum geology, oil well completion and cementing, drilling processes, refining, production and stimulation and other production processes. Through the impulse of ideas and innovations in the field of nanotechnology, oil and gas industry will receive high boost by exposing the equipment materials to extended work conditions. Also, the advancement of nanotechnology which is related to a very good simulation tools enables the characterisation of interfacial processes between fluids and minerals (flow control and wettability), giving a very good understanding of all the mechanisms for enhanced heavy oil recovery. Oil and gas industries are heavily investing in the areas of nanotechnology for improved reliability of equipment, enhanced heavy oil recovery, analytical emulsion characteristic, reduction in energy losses during crude oil processing and development of products with high performance.

II. Nanotechnology In Oil And Gas Industry

2.1 Enhanced Oil Recovery Using Nanotechnology

One of the outstanding features of nanoparticles is their high surface area to volume ratio, this enables them to pass through a porous media (pore throats) of a given reservoir. Notwithstanding, the nanoparticles cannot be trapped or retained by the rock (Abdelrahman, 2013).One of the major application of nanoparticle is in EOR, as the process provides large amount of oil during extraction and ensures a better return on investment. In the use of nanotechnology in oil and gas industry, different techniques have been considered and many appears highly promising. The application of nano-robots in oil well pad provides useful information to the operator for enhanced conduction of the drilling operations, a typical example is the dynamic adaptation of the operating pressures and additive mixtures.

Generally, Enhanced oil recovery is an advanced process which involves different chemical applications solely aimed at increasing the amount of crude oil which can be extracted from a hydrocarbon oil well/reservoir. This discipline has recently found its usefulness through the application of nanotechnology. Research has established the difficulty transportation of a colloidal dispersion in reservoir rocks (Yu *et al.,* 2010). This is because the colloidal dispersions are retained on the walls of the reservoirs, hence do not get to their target points where its applications are required. However, the small size of nanoparticles allows them to pass through the pore throats, but, their delivery at the target points where there is existence of oil within the rock needs more emphasis. This is a clear indication that nanoparticles support the enhanced heavy oil recovery processes.

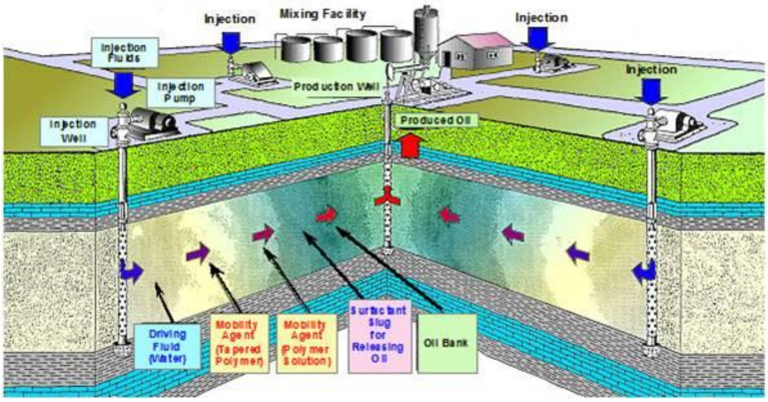

Figure 3: Chemical flooding method for Enhanced Oil Recovery (Ogolo*et al.*, 2012)

According to (Yu *et al.*, 2010b) the transport and retention properties of aqueous dispersions of paramagnetic nanoparticles in reservoir rock were studied. Surface treated paramagnetic iron-oxide nanoparticles at concentration of 0.1e10% wt. were considered for the core flood experiments. In the work of (Yu *et al.*, 2010) the transport and retention properties of nanoparticles through dolomite and sandstone cores were investigated at high salinity condition. They considered carbon nanoparticles with/without surface treatment, and so, the effect of surface treatment was also studied. Dolomite is known to be positively charged owing to its large amount of divalent ions of calcium and magnesium (Ca^{2+} and Mg^{2+}), while sandstone is negatively charged due to its predominant silica content (Yu *et al.*, 2010).

The results of the core flood experiments (when carbon nanoparticleswithout surface treatment was used in the presence of(KCl, Ca^{2+} and Mg^{2+} and seawater) revealed that nanoparticlesbreakthrough was delayed. The delayed breakthrough was areflection of carbon nanoparticles retention on core surfaces, aresult that arose from the effect of ionic strength and divalentions. It has been established in literature that a high ionicstrength (at increased salt concentration) leads to the shrinkage of the double layer of charged particles in aqueous suspensions, and consequently, reduces their repulsive capability (Yu *et al.*, 2010; Tadros, 2013 and Ali *et al.*, 2004). The retention is greater with dolomite cores than with sandstone cores (Yu *et al.*, 2010). This is because of the additional attractive force that emerged between the negatively charged carbon nanoparticles and the positively charged dolomite surface, unlike sandstone that has negatively charged surfaces. The breakthrough values recorded with surface-treated carbon nanoparticles were relatively higher compared to the ones obtained with untreated nanoparticles - a confirmation of minimal retention. The surface modification assisted in shielding the carbon nanoparticles, and thus, inhibited charge interaction. This explains the reason behind the use of surface-treated nanoparticles in most of the research reported in publications.

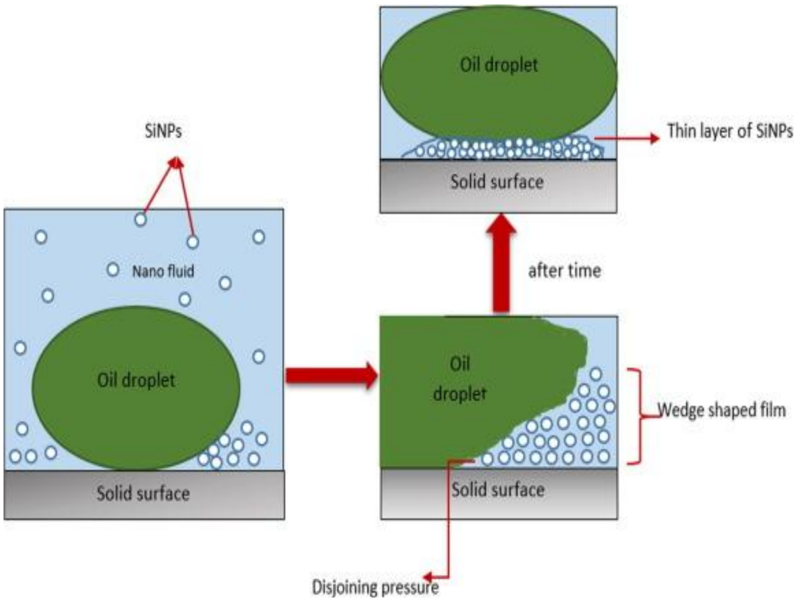

Figure 4: Nanoparticle structuring in the wedge-film resulting in structural disjoining pressure (Abdelrahman Ibrahim El-Diasty, 2013)

Enhanced oil recovery is guaranteed by dispersion of nanoparticles in a suitable fluid. From the research work of Ogolo*et al.,* (2012) for enhanced oil recovery experiments. He used different nanoparticles such as aluminium oxide, magnesium oxide, tin oxide, zirconium oxide, nickel oxide, tin oxide, iron oxide, zinc oxide, hydrophobic silicon oxide and silicon oxide which was treated with silane showing enhanced recovery and boosted hydrocarbon production. The use of these nanoparticle oxides are highly related to the variation of rock wettability, interfacial tension reduction, oil viscosity reduction, reduction of mobility ratio and permeability alterations. Another example in nanoparticle use (in order to improve the oil recovery efficiency) as an additive for operations has been studied by University of Alaska Fairbanks (Rusheet, 2009) where some researchers highlighted the important performances guaranteed by the use of metal nanoparticles dispersed into supercritical CO_2, responsible of the heavy oil viscosity reduction with consequent increasing of recovery efficiency.

According to the research work of Rodriguez *et al.,* (2009); sedimentary rocks with different permeability and lithology was injected with a concentrated aqueous suspension of a surface enhanced silica nanoparticle of about 20 wt % (D = 5nm and 20 nm). The surface-enhanced silica nanoparticles in the aqueous suspension assembled themselves, forming a structural array at a discontinuous phase of the oil, gas or paraffin. This caused a formation of a wedge-like structure by the particles present in these three-phases of contact region, forcing themselves through the discontinuous phase and the substrate as shown in figure 4.

2.2 Corrosion and Scale inhibition

Corrosion and scale formation is a very big threat to production equipment. Corrosion and scale formation causes the destruction of metallic parts. It is of great need to remedy the occurrence of these defaults in oil and gas industries. Nanotechnology has proven as a way forward for researchers in circumventing these effects. Many researchers have proven the use of nanotechnology for corrosion and scale inhibition (Jauhari*et al*., 2011 and Murugesan*et al.,* 2016). In the research work of Murugesan*et al.,* (2016), the preparation of nano-magnetic fluid was carried out by suspension of a ferromagnetic nanoparticle in a carrier-fluid. This medium was very effective in reduction of scales and corrosions levels on a carbon steel in acidic medium. In oil and gas industries, metallic conduits are used for the transportation of acids which exposes their surfaces to various chemical reactions that causes scaling and corrosion.

However, when the acids transported through the metallic conduits are blended with corrosive inhibitors, the scaling and corrosion of the process materials will be greatly inhibited. The ferromagnetic nanoparticle used for the experimental work ranges from 3-15 nm, and 0.1M solution of nitric acid was used as the acidic medium. The weight loss was measured using a gravimetric analysis. This was done through the suspension of a carbon steel in the nitric acid, this was carried out at varying concentrations of nano-magnetic fluid inhibitor. Also, the polarization and its electrochemical impedance were calculated a steel specimen of $1cm^2$ surface area which was exposed to the test solutions with or without the concentrations of the nano-magnetic fluid. From the result, the rate of corrosion and percentage inhibition efficiency measured from the weight loss, decreased and increased respectively as the concentrations of the ferromagnetic nanoparticles increases. In summary, it was shown that, ferromagnetic nanoparticles inhibit corrosion and scaling as they adhere to the carbon steel surface forming a very protective layer.

Nanoscale modification of surfaces has been recommended by Kazemi*et al.*, 2012, that it prevents adhesion of scale on rocks. From this research, it was shown that organo-silane has the ability to directly inhibit the formation of scales. The formation of self-assembled organo-silane films from solutions with varying concentrations expressed differences in film thickness and in scale deposition on the films. This indicates the presence of different structures having varying ability to inhibit scale deposition; in turn, it also suggests the need to characterize such films for scale inhibition purposes.

Kumar *et al*., 2012, expressed new sight which can greatly prevent the formation of scales inside the production tubes through the creation of super-hydrophobic surface with many scale nano-structures on the tubes. The use of dip-coating processes on the epoxy pain surfaces, helps in the creation of the surfaces. Nano-structures are further incorporated on the micro-surfaces by the addition of 50-100 µm SiO_2 nanoparticles and completed by dip-coating with a solution of nano SiO_2/epoxy adhesive. The enhancement of the hydrophobicity is done by further dip-coating with polyaminopropyl (a low surface energy polymer). The super-hydrophobic surface indicated a contact angle of 167.80 degrees (Cui *et al.*, 2009) for water, with high stability in basic and some organic solvents (Kumar *et al.,* 2012).

2.3 Drilling and Hydraulic Fracturing Fluids Development using Nanotechnology

During drilling processes, drilling fluids are majorly used to transport drilled cuttings from a wellbore to the surface. Also, at the fractured zones of reservoirs, hydraulic fracturing fluids are used to carry the proppants into the fractured zones. These fluids also perform many other functions such as ensuring successful fracturing operation. The use of nanotechnology as it has been consistently researched, leads to a better development of these fluids. In petroleum industries, most fluids used contain micro and macro sized particles. These particles cause lots of damages to the process equipment. As described from the research work of Amanullah*et al*., (2011), he explained that the developed smart fluids with a nanomaterial highly enhances the formation of tight and thin mud cake, improving and enhancing filtration and rheological properties of the fluids. If the quality of the drilling mud is low, it leaves thick mud cake on the wall of the well-bore which causes increase in required force that could remove the drill-string, in case differential sticking occurred (Outmans, 1958).

Amanullah*et al.*, (2011) prepared water based nano-fluids with three available commercial nanoparticles at 0.5 ppb (0.14% w/w). At the dispersing phase, the enhancement of the viscous and filtration properties and the stability of the nanoparticle in the fluids, were maintained through the addition of a tri-functional additive and a vis-cosifier. For comparison, a sample of bentonite mud was prepared having a micro-sized particle. The stability of the nanofluids were confirmed through the measurement of their gel strength and viscous properties with a rotational viscometer at 18, 48 and 72 h. Results obtained were very close. This showed the stability of the nanofluids used and had the potential to meet field application requirements. The nanofluids, compared to the bentonite mud, had a better viscous property and they exhibited a constant gel strength (i.e. the 10 s and 10 min gel strength were identical). But, the API (American Petroleum Institute) fluid loss characteristics of the nano-fluids and bentonite mud displayed a similar trend; but, no spurt loss was recorded for the nano-fluids. The mud cakes produced by the nanofluids were thin and tightly packed, and with a thickness of less than 1 mm.

At the post-treatment stage, the combination of surfactant in brine and nanoparticles which contains internal breaker will enhance the removal of polymer residues from hydraulic fracture (Crews and Huang, 2010). These internal breakers are trapped in the thread-like micelles (TLM) that form the pseudo-filter cake, and in those that leak into the formation (Crews and Huang, 2007).

There are research reports on the use of nanoparticles as a crosslinker of fracturing fluid as they enhance the build-up of viscosity (Harnaus and Plank, 2015). Also, fracture conductivity that is related to a croosslinked polymer fluid is yet to be resolved (Crews and Huang, 2010). From the research carried out for the fracture conductivity of a crosslinked polymer fluid named particle park flow tests (i.e. flow tests through particulate media), involved the loading of the flow cell with different sizes of sand proppants. In these tests, the remedial cleanup fluid used was a mixture of 3% KCl brine, 0.072% wt. Cx40 nanoparticles (of approximately 35 nm size inorganic crystals), 1 and 3% wt. gel-forming surfactant, and 0.18 and 0.25% wt. polymer breaker E-21. Particle park flow tests showed a reasonable resistance to fluid flow, even at a condition of a low surfactant concentration in high-permeability medium. The effectiveness of internal breaker was proven by examining the viscosity of effluent collected after post-flush. The viscosity took water-like nature due to the degradation of TLM structure by the internal breaker and removal of more polymer residue. The degradation caused the rearrangement of the structure of TLM into non-viscous spherical-shape micelle structure as depicted in Figure 5.

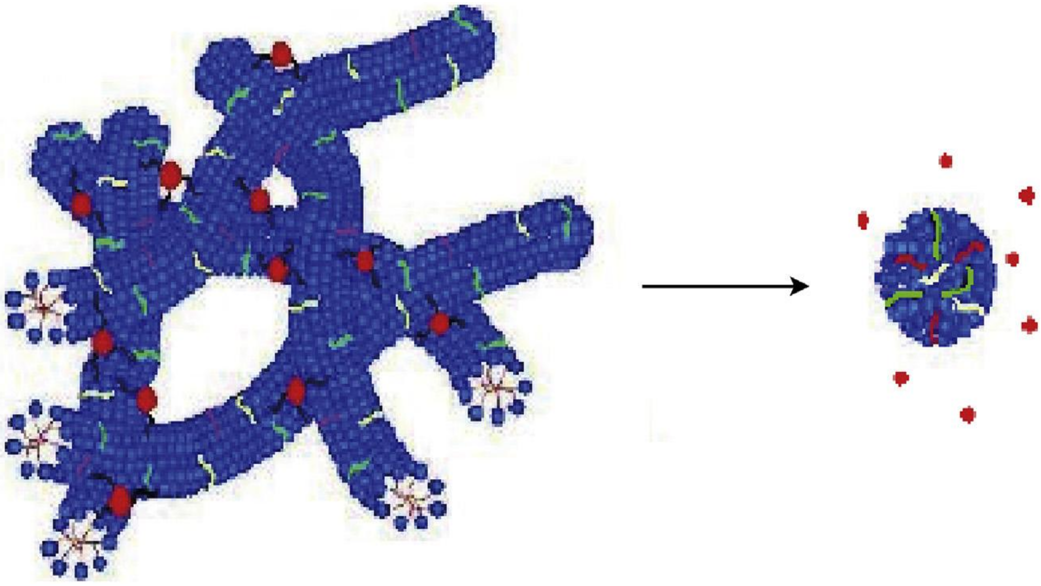

Figure 5. Degradation of TLM structure by the internal breaker (source: Crews and Huang, 2010).

2.4 Exploration and reservoir characterization

In oil and gas industry, exploration and reservoir characterization is one of the essential unit operation, yet expensive and high risk exposed. Its aim is to locate hydrocarbon accumulation beneath the earth's surface. However, this process always presents a lot of challenges such as unexpected geological aggregation of the hydrocarbon and unanticipated hazards, these in turn greatly increases the cost of hydrocarbon production. Research revealed that conventional sensing methodologies with exception to ''seismic technique'' always provide limited information about reservoir characterization, owing to the fact that they could only penetrate few inches through the wellbore. Current sensing technologies lacks the ability to accurately penetrate deeply into the wellbore, thereby providing poor results on the resolution imaging of the reservoir. Also, at extreme condition of the reservoir, conventional sensing devices cannot ascertain information about the device.

Nanotechnology/Nano-sensor over conventional sensing technique is a new, very sensitive, low cost, simple and non-damaging technique. Owing to the virtue of their size dependent, chemical, optical, magnetic, electrical and catalytic properties of nanoparticles, they can easily be implemented into a nano-sensor which can easily penetrate through the pores of the geological structures for good resolution and imaging of the reservoir. Nanotechnology is also used in probing the nature of association between rocks contained in a deeper reservoir. This explains the complex interaction between the reservoir rocks and fluids, checking if there are immiscible fluids distributed across the rock.

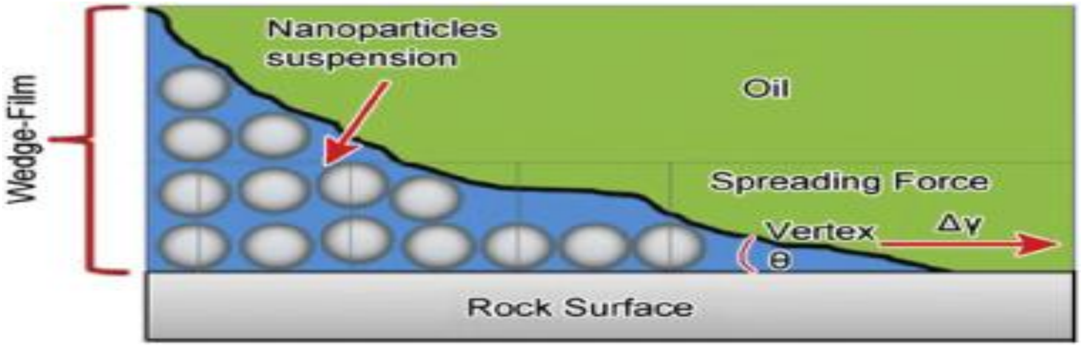

Figure 6: Scheme for exploration and reservoir drilling using nanomaterials (Ogolo*et al.,* 2012)

Exploration of hydrocarbons in an electromagnetic based reservoir is often carried out using a magnetic nanoparticle. This is often preferred over other nanoparticles because, magnetic nanoparticle reduces the magnetic permeability of rock formation in a reservoir and enhances high imaging resolution magnetic measurement at a very low cost. Other application of nanotechnology in exploration and reservoir characterization is the development of innovative nanomaterial based sensing device, primarily for monitoring substances such as pollutants, toxic and hazardous gases. These pollutants include CO_2, H_2S and other forms of natural gases such as CH_4 (Saidur*et al.,* 2011; Metin, Baran and Nguyen, 2015).

2.5 Cementing

This is a process of preparing well for further drilling and oil production. Cementing a well is the procedure of developing and pumping cement into place in a wellbore. Most commonly, cementing is used to permanently shut off water penetration into the well. Oil well cement is generally used for this process. They usually consist of Portland cement with special organic retarders to prevent the cement from settling too quickly. During drilling operations, so many challenges set-in inside the wellbore such as wellbore failure, incomplete cementing, formation damages due to drilling operations, inadequate cement formation, cement shrinkage, filtration of cement slurry, incomplete cement placement, contamination of cement by drilling fluids and fracture formation. All these affects the integrity of the oil-well. Also, during production challenges like cement failure due to mechanical or thermal stress, corrosion of casing, degradation of cement due to carbonation, sulfate or acid deposits may significantly lower the oil production. Therefore, the selection of cementing materials as well as cementing procedures plays a key role to ensure the success in oil and gas exploration and production. Research has revealed the use of a nano-sized smart materials as an additive in cementing with desired specific properties (Harnaus and Plank, 2015). The use of nanomaterials such as carbon nanotubes and nanoparticles like TiO_2, Fe_2O_3, Al_2O_3, ZrO_3, CuO and ZnO_2 in cementing helps in strengthening and increasing durability, resistance to water penetration, acceleration of hydration reaction, control calcium leaching, improves the impact and fracture toughness, enhances dry shrinkage and permeability resistance properties (Yu *et al.,* 2010).

2.6 Production and Stimulation

Recovery from the unconventional resources such as heavy oil, shale gas and liquid, tight gas and oil, coal bed methane and bitumen hydrocarbons has been one of the major current challenges in oil and gas production. Years back, most companies are investing in unconventional resources due to shortage in the conventional oil reserves. According to literature, there are about 5.6 trillion barrels of unconventional heavy oil which is about 1.02 trillion barrels higher than conventional light oil in the world (Xiao *et al.*, 2015). The current recovery technologies before the emergence of nanotechnology can only recover about 650.70 billion barrels of these unconventional heavy oils (Harnaus and Plank, 2015).This is due to the nature of physical and chemical properties as well as the geological difficulties of the unconventional heavy oil. The emergence of nanotechnology has enhanced efficient and effective harvesting of these unconventional heavy oil. However, this is carried out by using several types of nanocatalysts and nano-sized transition metals in a process called ‘‘Aquathermolysis’’.

2.7 Aquathermolysis

Heavy oil is known to be rich in heavier organic compounds such as resins and asphalthenes. They are richer in compounds with at least 60 carbon atoms, in addition to heterocyclic derivatives. These mixtures resulted to high physico-chemical characteristics such as high viscosity, high boiling and molecular weight. These poses serious recovery difficulties. The mobility of the oil is seriously restricted and therefore displacement by simple fluids like water or gas became inefficient. For these reasons, recovery factors become limited. A number of interesting options are being considered for enhancing the recovery efficiency.These options include: microbial recovery, thermal recovery, chemical recovery and steam recovery. Generally, these recovery methods are associated with problems that limited their reliability. An alternative being considered is a process called aquathermolysis.

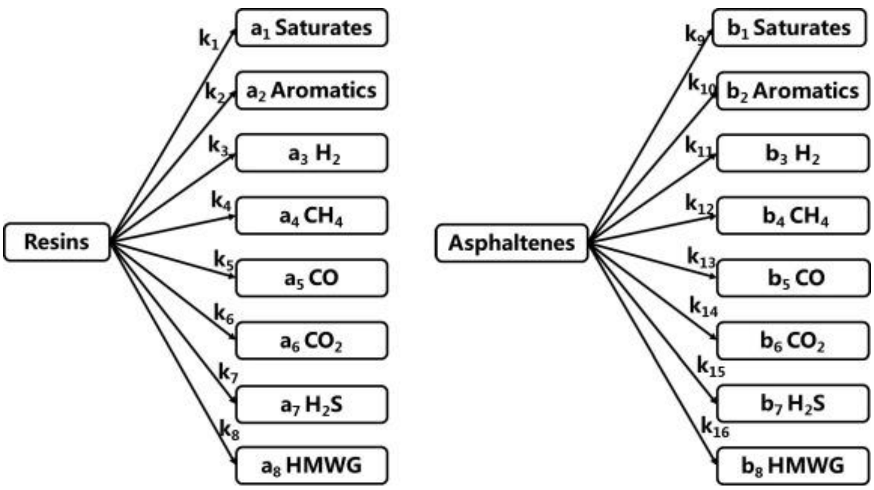

Figure 7: Aquathermolysis process in breakdown of Resins and Asphaltenes.

This generally involves the degradation of unconventional heavy oils by the use of nanocatalyst and nanoparticles which helps in reduction of the viscosity of the heavy oils containing higher molecular weight hydrocarbons such as asphalthenes and resins. Research also showed that hydrogenation, hydrodesulphurisation, Hydrodenitrogenation and hydrocracking are the major reactions taking place during aquathermolysis. Also one of the major reason for this process is the bond cleavage of N, S, O containing compounds in the petroleum fraction.Aquathermolysis results in irreversible lowering of heavy oil viscosity at temperature ranges from 200˚C - 300˚C(Abdelrahman, 2013). According to VBT, among C-O, C-S, and C-N chemical bonds, the C-S bond energy is the least. Because of this, the C-S bond will break in the process of Aquathermolysis and result in a low amount of sulphur and heavy components such as resin and asphalthenes. The hydrolysis of aliphatic sulphur linkages is the main characteristic of these reactions

R-S-R + H_2O …………………. CO + H_2S + Lighter organic compounds

Hydrolysis is achieved by transferring hydrogen from water to the oil via WGSR

CO + H_2O ………………….. CO_2 + H_2

Clerk et al., (1990) noted that using aqueous metal salts instead of water in steam stimulation improves the properties of the recovered oil such as viscosity and asphalthene content. The observed improvements are due to the catalytic effect of the metals on the aquathermolysis reactions which can further upgrade heavy oil under steam stimulation.

2.8 Conclusion, Challenges and Research gaps

A well detailed review of the applications of nanotechnology to various areas of oil and gas industry has been comprehensively reviewed in this paper. The application of nanotechnology in oil and gas industry has completely changed the current practice in exploration and production of hydrocarbon. This area has gained rapid development in synthesis and application of a smart nanomaterials in oil and gas recovery. However, there are still current challenges in the application of this process. One of these challenges is the search for cost effectiveness and simpler synthetic route. Most of the current synthetic routes are dependent on equipment that are cost ineffective and some materials that are not environmentally friendly. A cost effective route for synthesis and delivery of nanomaterial is of research interest.

Due to lack of agreement of results from various studies, poor characterization of data and lack of lucidity of the basic mechanism responsible for migration and transport behaviour of nanomaterials across porous medium, it has pose itself as a challenge in the use of nanoparticles in oil and gas industry. Also, effective determination of the size of nanomaterials to secure effective penetration in porous reservoir medium containing crude oil is of high research interest.

Coarse and rough subsurface conditions is also a contributing challenge in the later application of nanotechnology in oil and gas industry. Nanomaterials at extreme coarse and rough conditions easily agglomerate. This causes increase in the particle size there by losing their unique size properties. However, this problem can be solved by surface coating of all the nanomaterials with a polymeric substance which can reduce surface adhesive interaction. This practice greatly reduces the enhanced specialized properties of the nanomaterials such as their sensing abilities, catalytic properties, rock wettability effect, etc, this suggests that a better approach is required.

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