ISSN: 0976-3031

International Journal of Recent Scientific Research

Impact factor: 5.114

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Volume: 6

Issue: 9

THE PUBLICATION OF
INTERNATIONAL JOURNAL OF RECENT SCIENTIFIC RESEARCH
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International Journal of Recent Scientific Research
Vol. 6, Issue, 9, pp.6161-6166, September, 2015

International Journal of Recent Scientific Research

ISSN: 0976-3031

RESEARCH ARTICLE

APPLICATION OF NANOTECHNOLOGY IN PETROLEUM INDUSTRY

Ananthu Mahendranath., Sunil Varkey and Sonal Mazumder*

Department of Chemical Engineering, Birla Institute of Technology and Science, Pilani Rajasthan

ARTICLE INFO

Article History:

Received 05th June, 2015
Received in revised form 08th July, 2015
Accepted 10th August, 2015
Published online 21st September, 2015

Key words:

Advanced Energy Consortium, Wettability, Nanomaterials, Enhanced oil recovery, Nanofluids, Interfacial tension, Rheology

ABSTRACT

As the demand of petroleum and its products are increasing enormously, the huge growing need is putting substantial pressure on petroleum industries. Although nanotechnology is not completely new to the oil industry, its application was very limited until recently. The application of nanotechnology has massive potential for revolutionary changes in petroleum industries covering wide areas of the upstream and downstream process. The paper gives an overview of the most common areas where nanotechnology has been applied for petroleum industries and also passes through its significance comparing to the conventional methodologies. The paper also states some very interesting case studies on enhanced oil recovery and results produced by the application of nanotechnology from all over the world.

INTRODUCTION

The demand for energy is expected to increase around 50% to 60% in the next 2-3 decades. According to a study by the US Department of Energy, the predicted global energy consumption will be around 700 Quadrillion British thermal units by 2030 [1]. Renewables, from wind, solar, small hydro and geothermal, is expected to grow at over seven per cent per year, often as a result of government support and incentives. They certainly hold promise, but globally their share of the energy mix will still be less than three per cent by 2035, given their low initial base. Both the share of biomass and nuclear remain at steady levels throughout the period from 2010 to 2035, at around nine per cent and just below six per cent respectively. It is clear that fossil fuels will continue to play the dominant role in meeting demand, although their overall share will fall from 82 to 80 per cent. Throughout most of this period, oil will remain the energy source with the largest share, although its overall share declines from 33 to 27 per cent. [2]. Unless, revolutionary new sources of energy have been industrialized, yet it appears that we are going to be reliant on hydrocarbons for the foreseeable future [3]. With peak oil demand fast approaching, there is a definite need to be able to fully utilize all of the resources that are available.

In the petroleum industry the reservoir is not something like a tank, which most of the people visualize, but it is solid rock. Oil is trapped in numerous tiny pores within these rocks and travels between the pores through small passageways called pore throats, which are even smaller than the pores. So it requires much more effort to recover more oil after using natural mechanisms or artificial lift devices such as pump jacks. The nanoparticles, i.e. those that are in the size range of one billionth of a meter, has a crucial role to play, whether it is to push oil out of these pores or to know more about the environment down there.

Nanotechnology is the science of manipulating and controlling matter with at least one dimension sized from 1 to 100 nanometers, as defined by the National Nanotechnology Initiative. The nano science and its importance have grown so rapidly in the recent time. It has been put to use in numerous fields including medicine, electronics, communication and coatings. In the past few decades wide possibilities of application of nanotechnology were reported in the petroleum industry and have produced amazing results.

Compared to other industries, the nano technology applications have been put to limited use in oil industries. However, in the coming years, it is expected that with the help of

Corresponding author:* **Sonal Mazumder
Department of Chemical Engineering, Birla Institute of Technology and Science, Pilani Rajasthan

nanotechnology, materials with unique properties such as lighter structure, stronger structural composites, low maintenance coating, better properties of cementitious materials, improving pipe joining materials and techniques can be produced.

The major challenges faced by petroleum industry include quick wearing down of drilling equipment, major left out volumes of unrecovered oil inside the reservoir, inability of the existing seismic technology to provide better understanding of the reservoir. For the past few years, many new promising applications of nanotechnology in the petroleum industry have been reported from different parts of the world. Some of the most general ones are discussed in below section.

Sensors

The Advanced Energy Consortium (AEC) was constituted in US during 2008 with the task of exploration of nanotechnology in oil and gas industries [4]. Their primary goal was to produce nano sensors which could be injected in the oil wells. According to various studies, it has been shown that nano materials yielded better results when used in the production of sensors and other imaging techniques. It is due to the significant alterations in the mechanical, magnetic, optical properties of the materials. Such materials are usually combined with smart fluids which can be used as highly sensitive downhole sensors to detect the variation in temperature, pressure and stress. It is considered that nano robots will be the future in imaging and sensing [5]. Nanorobots could provide effective reservoir mapping, although it's still a dream. The studies about the multi phase flow of fluids carrying nanomaterials through porous media are the major focus in petroleum research.

At the current scenario, the oil and gas industries measure the changes in temperature and pressure at the wellbore. The aim of the AEC is to enable direct measurements kilometers away from welfare. For this AEC is initializing three methods [6]. In the first method, ultra small electronic sensors are sending to the downhill and the data are collected by recovering them. The aim is to develop nanoscale electronic sensors which can even move through the pores of rocks and not just the perforations or fractures.

The second focuses on developing electronic sensors with chemical equivalents which can go much deeper into formations. In such a method the scientists are expecting the nanoscale reporter to get exposed and retrieve data once it reaches a particular region of interest. Hence the nanoscale reporter is confined in a capsule which will degrade as it moves down the reservoir and finally expose the reporter once it reaches the exact region. The final method uses contrasting agents which helps in tracking the movement of fluids during waterfloods and completion. These are mainly used in cases where the sensors and reporters would be impractical. The contrasting agents are added in the front of the flood and hence it will have a higher electromagnetic signal than the rest of the flood. With the usage of geophysical tools one could capture electromagnetic image and track the motion of flood.

Coatings

Initially nano coatings were considered to be used as a protection for steel structures. This coating incorporates certain characteristics to the steel structures such as corrosion resistance, wear resistance, enhanced thermal conductivity and shock resistance [7]. Corrosion is a huge problem in any industry which halts production and consequently cost repairing. A coating consisting of 30% of water based acrylic resin and 70% of nano composite along with nanometer tunnel covers the oil, transmission pipe completely and ceases any scope for air penetration [8]. But with the advent of more intensive research in the field it was found to add much more than the conventional uses. The research focuses now on the transition of multifunctional nano-polymer coatings from lab scale to commercial applications. This includes the application of nano coatings as a protection against external agencies, along with combination as a sensor which can respond to the mechanical, chemical and physical changes on the surface. In the future one could also expect a self healing nano coating with the advancement of nano encapsulation. The coating using carbon nanotubes is getting ready to be marketed soon which has the ability to conduct current for the evenly heated surface. This can be used to prevent gas hydrate formation (solid crystalline compounds of snowy appearance) in pipelines which causes plugging during transport of oil [9].

DRILLING FLUIDS AND MATERIALS

Drilling fluids are majorly used for lubrication and as a coolant for a drill bit. The features of nano materials enable to add unique characteristics compared to the parent material. They are more efficient in removing rock debris, drill cutting and are considered as the smart fluids which can empower the performance compared to the conventional techniques [7]. Due to the exceptional property of high surface to volume ratio in nanomaterials, they can exhibit high interactions with the surroundings even when their concentration is less. The smart fluids enhance drilling by wettability alteration, mobility control and sand consolidation.

The major solution to the drilling problems like erosion of borehole, mud sticking to the pipe, thermal instability of drilling fluids and lost circulation lies in the proper manipulation and control of the rheological property of the fluid. The clay composite water based bentonite is one of the common drilling mud compositions. Its performance is evaluated by exposing the composition to varying temperature and pressure. The study found that the temperature had an adverse effect on the rheological properties of the fluid. Further studies using synthesized nano bentonite drilling fluids gave exceptional results [10]. At all elevated temperatures and pressures, the rheological property of the fluid remained stable. This phenomenon is due to the better and improved density and viscosity of nanomud with less roughness.

With the advent of synthesis of elastomer composites with carbon nanotubes, stronger, lighter, tougher and more resistant drilling equipments can be manufactured. In the coming years, there is potential for these equipments to be combined with self sensing elements. The use of nano structured dispersed hardened materials produces very hard materials. Examples are the diamond poly crystalline nano composites and boron nitride nano composites [5]. For improving hydraulic fracturing, nano structured metal composites are combined with magnesium, aluminium, and other alloys which imparts strength with lesser weight and more durability.

Concrete

Concrete is one of the most dominant materials during construction of reservoir wells. Addition of nano materials to cement drastically improves its performance. Nano silica, nano alumina, nano-Fe_2O_3 have been extensively used with cement to improve its compressive and flexural strength [11-13]. It's also found that adding 1% of carbon nano tubes add to the compressive strength [14]. Novel super plasticizers, nanoparticles, or nano reinforcements are the new type of cement additives. The fundamental cement structure can now be altered using various methodologies for hybridization and by grafting of molecules which allows direct manipulation.

Nano silica is the extremely fine silica particles which are added to cement admixture in oil and several other construction industries. Due to its fine form and high reactivity, it helps in the improvement of mechanical properties in cement concrete. Adding 1% of nano silica to slurry admixture was found to be the optimized value of improved properties. The advantage of adding nanosilica to drilling cement mixture includes very low porosity and permeability, high compressive strength, reduction in thickening time and lessens fluid losses [15]. Nano-SiO_2 has found application very close to cement degradation by controlling the leaching of calcium. Nano-SiO_2 is also used as a resistance to water penetration and improving concrete workability and strength. Whereas, Nano-TiO_2 proved very effective for self cleaning of concrete and subsequently helps to clean the environment [16].

Nano Membrane

The nano membranes are inspired from salts which are capable in the separation of the light and small gases such as nitrogen and oxygen. These membranes are lightweight, large scale, durable and sturdy. They are mainly used to enhance the separation or exploitation of tight gases by removing impurities, improving gas to liquid production and separation of gas streams [5]. Nano porous materials are another class which is used to remove environmentally hazardous gases such as hydrogen sulfide and carbon dioxide in hydrocarbon mixtures.

Recently, researchers have developed a ceramic nanomembrane which can efficiently dehydrate natural gas [17]. Its importance lies in the fact that the natural gases contain water, which condenses and finally forms solid gas hydrates, which can ultimately block pipelines and accelerate corrosion problems. This new membrane has high chemical and thermal stability and helps in significant reduction in energy consumption. These were synthesized on a base of porous ceramic made of alpha alumina. Although they have many pros, still nano membranes are in its initial stages of developments due to the high cost and reproducibility issues.

Enhanced Oil Recovery (Eor)

Even after employing primary and secondary methods of extraction, a typical oil well retains up to around 70% of the oil, i.e. by usual extraction techniques, we are only able to extract one out of three barrels of oil from a well. This is why we have to employ EOR techniques to increase the output from a given well. In the recent past many promising applications of nanotechnology in EOR have been reported across the world. But most of them are still only in the lab scale studies. Some of these are being discussed in brief here:

Roustaei Abbas *et al* (2012) reported a work on modified silica nanoparticle's efficiency in enhanced oil recovery of light and intermediate oil reservoirs [18]. Their studies revealed that modified silica nano fluid improved oil recovery through major mechanisms of interfacial tension reduction and wettability alteration to more water-wet from oil-wet condition and more pronounced observation was found in the case of light oil reservoir. Partially hydrophobic fumed silica was used for the study.

Oil phase contact angle of sandstone plates showed a decrease from 135.5^o to 66^o in the case of light oil and from 130^o to 101^o in the case of intermediate oil, after surface treatment with modified silica nanoparticles. They are anticipating the change in the free energy of the sample plate surface due to adsorption of nanoparticle and fluid- fluid interaction in the presence of nanoparticle as the reason for the phenomenon. The reduction of the interfacial tension between water and oil will allow recovery of oil trapped in the smaller pores and part of the residual oil remained in the pores after water flooding. This will ultimately lead to a reduction of the capillary pressure within the pores, which was preventing oil from flowing through the rocks. The wettability alteration changed the role of capillary force from a barrier to a driving force that squeeze a hydrocarbon droplet through a pore throat. The study showed employing nano fluid lowers oil–water interfacial tension from 26.5 mN/m to less than 1.95 mN/m for the light oil system and from 28.3 mN/m to 7.3 mN/m in the case of the intermediate one.

Reduction of interfacial tension reduces the work of deformation needed for oil droplets to move through the pore throat. A possible explanation for the reduction of interfacial tension is adsorption of nanoparticles-ethanol complex at the interface, replacing the water and/or oil molecules of the original interface. This lead to the interaction between the hydrophilic part of the complexes and water molecules on one side of the interface and between the hydrophobic part of the complexes and oil molecules on the other side of the interface. Since these interactions are now much stronger than the original interaction between the highly dissimilar oil and water molecules, the tension across the interface is reduced by the presence of the nanoparticle- ethanol complexes [19]. The oil recovery was increased by 25.43% and 14.55% respectively in the light oil sample and intermediate core sample after the injection of nano fluid. The capability of nano fluid in enhancing oil recovery depended on the oil type and varies for different oil reservoirs. The researchers assume that the nano fluid must have reacted with both rock and reservoir oil. It is

proposed from the fact that there was a change in color obtained from the effluent fluid from the core plug. There were also significant contact angle and interfacial tension variations.
Ehtesabi H *et al* (2014) reported the behavior of low concentration of TiO_2 nanoparticles in core plug porous media and the mechanism of increasing oil recovery [20]. TiO_2 nanoparticles, an inexpensive and environmentally friendly material, are structurally stable towards high pressure and elevated temperature since it was synthesized without surfactants or polymers for modifying or coating the nanoparticle. The photocatalytic property of TiO_2 can effectively degrade oil pollutants in the presence of solar radiation which adds to its value. The nanofluid should be stable against high salinity, elevated temperature and pressure without causing aggregation. It should be able to propagate a long distance deep into the reservoir between the injection and production wells and also should get adsorbed to critical sites inside the reservoir like oil/water interface. The deposition must be of monolayer and overdeposition should be avoided.

Alaskar *et al* (2011) showed that the transport of nanoparticles through porous media is influenced by size, shape, and surface charge of the particles [21]. The TiO_2 nanoparticles synthesized where in antase crystalline phase with around 58 nm in size and showed stability upto 48 h. Nanofluid flooding tests showed that a 0.01% TiO_2 nanofluid gave a better oil recovery compared to 0.05% TiO_2 nanofluid which was way better than 5000 ppm brine. Also the oil recovery got saturated after sometime for brine whereas in the case of nanofluid it continuously increased with its injection. The material balance of the injected nanofluid through inductively coupled plasma (ICP) experiments showed that the concentration of nanoparticles decreased with distance inside the core. It was also seen that there was only negligible amount of TiO_2 in the outlet fluid indicating that most of it got deposited onto the rock surface.

The study proposed three main mechanisms through which EOR is accelerated by addition of nanoparticles to injection fluid. The mechanism includes increasing the viscosity of injected fluid, decreasing the interfacial tension between the oil and injected fluid, and changing the wettability of the rock surface from oil-wet to water-wet. Out of these only the third one had a significant contribution to explain the process as the results showed that TiO_2 nanoparticles do not change significantly the viscosity and the interfacial tension. The change in wettability of the rock from oil-wet to water-wet was confirmed using contact angle tests.

Wasan D *et al* (2014) reported EOR with the help of nanoparticle dispersions [22]. They utilised their specially formulated nanofluid - Illinois Institute of Technology (IIT) nanofluid which is designed to survive in high-salinity environment. Their work verified structural disjoining pressure mechanism for displacement of crude oil from rock and glass substrate. They showed the role of nanofluid in displacing crude oil from rock, especially in a high-salinity environment containing Ca^{2+} and Mg^{2+} ions. Their proposed mechanism for increase in oil recovery is due to the decrease in the interfacial tension and change in the flow characteristic of nanofluid moving from a Newtonian to non- Newtonian state.

Tour J M *et al* (2014) designed a nanoreporter that check for and reports on the presence of hydrogen sulphide in oil and natural gas inside the reservoir [23]. The amount of H_2S is estimated quantitatively from the change in the fluorescent properties of the injected polyvinyl alcohol with fluorescent probe-carbon black based nanoparticle. These nanoparticles showed efficient mobility and thermal stability under simulated downhole environments thus yielding promising results in both laboratory rock columns and in actual oilfield rock containing natural oil. Presence of H_2S has a direct impact on the quality of crude oil extracted. Its amount gives a rough estimate of the amount of sulphur present. The so called sour crude (crude oil with sulphur content greater than 0.5%) is toxic and can corrode the pipeline and other transportation vessels. Knowing the amount of H_2S gas in the reservoir in advance will be very helpful to take precautionary measures and more importantly it helps the geologists estimate whether the oil extraction from that well will be economical or not before large scale extraction.

A research team from The Research Council of Norway, reported a so called ‘nano-scale traffic jam’ for increased oil recovery. The method resembles that of selective plugging of pores using microbes[24] As water pass through the narrow tunnel-like passages which interconnects the pores, it squeeze its way through. If this injection water is infused with particles of size considerably lower than those tunnel diameters, then on reaching the tunnel entrance the water accelerates faster than particles leaving them behind which ultimately get accumulated, blocking the tunnel. As a result water will now start flowing through other pores which may have substantial amount of oil, thus increasing the oil recovery. The researchers founded elastic nanoparticles made of polymer threads which retract to coils as the best suited for the rock plugging rather than silica particles [25].

These experiments are few of the very enthusiastic and interesting works carried out by researchers on the effective application of nanotechnology in oil industries. These studies state the importance of nanotechnology in increasing the oil production, accurate detection of oil reservoir, cost effectiveness and better utilization of resources. It also promises a bright and hopeful future which is moving in the right direction.

CONCLUSION

The advantages due to the application of nanotechnology in oil industries are enormous. It clearly outweigh the little and negligible cons. Its success can have a huge impact on the exploration, production, refining, waste management and economics. Corrosion resistance, mechanical strength, durability, chemical and thermal stability, lightweight are some outcomes of the application in steel and concrete structures. Miniaturised sensors and robots give promise for exploration and detection of thin line pores in rocks. Zeolites and nanomembranes are in application for removal of tight gases and natural gas dehydration. Active research works are still on going through the world and many results have shown very productive results. But the main hurdle will still be the scaling up operations from lab scale or pilot plant study.

The future of nanotechnology seems to be very bright. There is no doubt that nanotechnology can provide satisfactory solutions to industrial problems which cannot be solved through conventional approaches. One only needs to have a look on how fast these technologies can produce the desired results with the growing demand of oil and its products. Hence long term research, substantial investment and a balanced time frame will make the perfect platform for a promising development.

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How to cite this article:

Ananthu Mahendranath *et al*., Application Of Nanotechnology In Petroleum Industry. *International Journal of Recent Scientific Research. 6(9), pp. 6161-6166,.*

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International Journal of Recent Scientific Research

ISSN 0976-3031