Investigating the Potential of Nanomaterial for Enhanced Oil Recovery: State of Art

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Abstract

Petroleum industry has been changed by the introduction of the nanotechnology. Nanotechnology has been tried in exploration. Drilling, production, and finally in enhanced oil recovery. For EOR, nanomaterials are considered an additive to the fluid used to displace the residual oil from the reservoir, which changes the characteristics of these solutions. These nano solutions have unique properties for a wide range of applications in oil field industry. There are several approaches for preparations of the nanomaterials; namely chemical and mechanical methods. Of course there a big difference between both of them and one can detect these variations by measuring its characterization and properties. From these methods, SEM, TEM, and EDX. The size and shape of the powder particles normally examined by x-ray diffraction (XRD) and scanning electron microscope (SEM) while their microanalysis are normally measured energy dispersive system (EDX). The initial stage used to investigate the performance of the nano materials for improving the oil recovery is normally done by displacing the crude oil in a flooding system and compare the final recovery factor to that of other EOR techniques such as water flooding or polymer flooding. The second step is to try to explain and interpret the results. This work offers an extensive literature review for assessing the applications of nano materials for improving oil recovery and investigating the current recovery problems, and then evaluating the potential technical and economic benefits that nanomaterials could provide to the reservoir engineering. Several nano materials are addressed and discussed. Moreover, it investigates the effect of nano materials on the relative permeability, the retention and loss of these materials inside the formation, and the numerical simulation of the nano material flowing in the pores.

Keywords: potential nanomaterial; enhanced oil recovery

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1. INTRODUCTION

Nanotechnology is the science of creating, using and manipulating objects which have at least one dimension in range of 0.1 to 100 nanometers. In other words, nanotechnology is reconstructing a substance using its individual atoms and arranging them in a way that is desirable for our purpose. The main reason that nanotechnology has been attracting attentions is the unique properties that objects show when they are formed at nano-scale. These differing characteristics that nano-scale materials show compared to their nature-existing form is both useful in creating high quality products and dangerous when being in contact with body or spread in environment [0].

Nanotechnology has been making its presence felt in oil and gas industry for some time, and many applications are already standard in petroleum refining. For example, nanostructured zeolites are used to extract up to 40% more gasoline than the catalysts they replaced. Meanwhile, for upstream operations, nanotechnology is helped for better materials. The oil industry needs strong, stable materials in virtually all of its processes. By building up such substances on a nano-scale, it could produce equipment that is lighter, more resistant, and stronger. Nanotechnology could also help develop new metering techniques with tiny sensors to provide improved information about the reservoir. Other emerging applications of nanotechnology in oil reservoir engineering are in the sector of developing new types of “smart fluids” for improved/enhanced oil recovery [[2]].

In 2011, Kapusta et. al. [0] stated that Nanotechnology has had an enormous impact in almost every industry, from consumer electronics to healthcare and telecommunications, but not in oil and gas exploration and production. Although nano-sized catalysts have been used in refining and petrochemical processes for many years, the use of nanomaterials and nano-techniques has only recently entered the upstream domain.

The largest impact within the upstream business is expected in subsurface applications, for instance contrast agents for advanced exploration and surveillance, novel fluids for enhanced oil recovery, and better analytical techniques for the characterization of oil and rock interactions.

Friedheim et. al. (2012) [0] in their paper titled “Nanotechnology for oil field applications – Hype or reality?” mentioned that the utility of nanotechnology in the oilfield is still a subject of discussion as well as debate. They reviewed the recent works on the application of nanotechnology in shale stabilization, high-temperature tolerance and viscosity modification, along with discussing the usage of grapheme, carbon nanotubes (CNT), nanosilica and other nano-chemistries to achieve and enhance the performance of drilling fluids. Then they concluded that there are several benefits of nano particles over colloidal or micro-sized materials. Figure 1 represents one of their results that had been discussed to prove the effectiveness of some nano materials used.

In 2010, Fletcher-Davis [0] mentioned that the Nanotechnology has the potential to transform EOR mechanisms and processes. Such processes at the nanometer – micrometer scale including wettability, coalescence, Marangoni phenomena, mass transfer effects and transient phenomena are related to EOR. They proved that oil phase distribution, oil drop mobilization, oil bank formation and oil bank migration cab be achieved for EOR processes.

In June 2012, Ayatollahi – Zerafat [0] postulated that using a nanoparticles (1-100 nm) brings specific thermal, optical, electrical, rheological and interfacial properties which are directly useful to release the trapped oil from the pore spaces in the order of 5 to 50 microns of tight oil formations.

In Egypt, geologic studies showed large reserves for white sand in different localities with good quality and available technologies for preparing products with different specification. Due to its high silica content (ranges from 98.5 to 99.6 wt%) the Sinai upgrading white sands products can be used not only for ceramic or conventional glass but also for optical glass, crystal, TV screen and silicon metal. It is reported that SiO2 nanoparticles as additives of lubricating oils could effectively improve the friction-reducing and anti-wear properties of base stocks, and the excellent synergism at a ratio of 0.25 wt% nano-SiO2. Nano silica particles have wide application in polishing [[7]]. Silica powders with high specific surface area were stable at high temperatures. When heated at different temperatures below 650°C, the specific surface area of the SiO2 powders hardly changed, therefore the SiO2 powders have better thermal stability [0]. (Liwei Wang, 1999). There is a growing interest in using nano-crystalline in the field of petroleum engineering specially for enhancing the recovery of the remaining oil after secondary recovery operations.

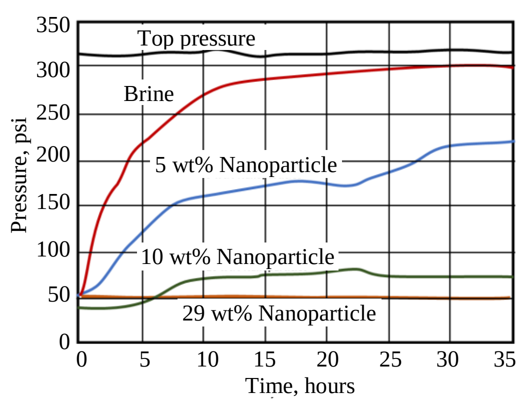

Figure 1: Sealing performance on Atoka Shale (Sensory et al. 2009).

2. NANO-MATERIALS FOR IOR

In May 2009, Kanj et. al. [00] detailed an experimental study on nano-fluid core flood experiments in the ARAB-D formation of the giant Ghawar field in Saudi Arabia. The study aims to test the feasibility and future reality for displacing molecular nano agents in the reservoir. Therefore, they performed a stability test in order to choose the best concentration and the conditions.

Wang et. al. 2010 [0] prepared a polyacrylamide micro-gel nano-spheres and they used them to enhance the recovery of Zhuangxi heavy oil (its viscosity is 238 mPa·s at 55℃,) in a sand-back model. They demonstrated experimentally that the promise future of Nano sphere in EOR. Their results achieved oil recovery over 20% OOIP after primary recovery on average. The final recovery ranges from 66% to about 78% after using nano fluid in the displacement. Figure 2 shows one of these experimental runs.

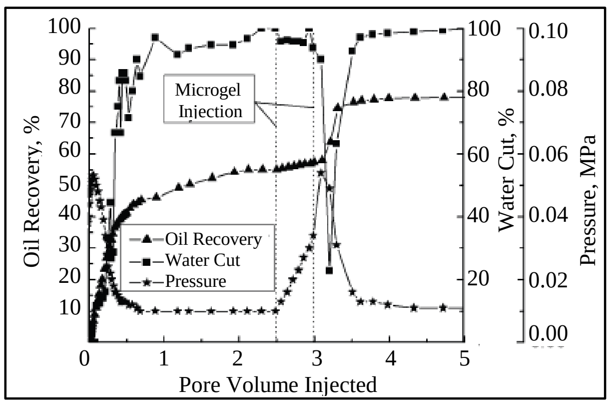

Figure 2: Cumulative oil recovery, water cut and pressure history of Run 3 (after Ref. 11).

Skauge et. al. (2010) [0] stated that the colloidal dispersion gels (CDG) for EOR providing sweep improvement in reservoirs with unfavorable mobility ratio (see Figure 3). Their work investigates the oil mobilization properties of nano-sized silica particles in comparison to nano-sized CDG particles. They presented a new concept of EOR by improved microscopic displacement defined as microscopic diversion. Based on their experimental work that was done on a Berea sandstone (500 md), they compared the performance of inelastic silica particles, polymer solutions, and nano-sized CDG particles.

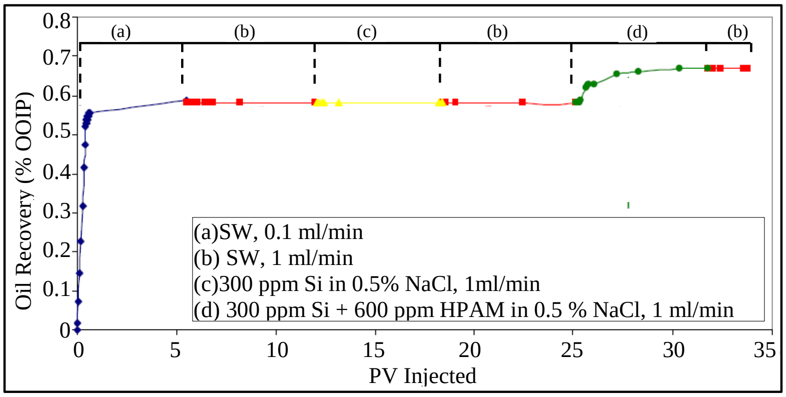

Figure 3: Oil production profile for the injection of 300 ppm silica and 600 ppm polymer in 0.5 % NaCl in Berea core B5[after Ref. 11]

Yu et. al. (2010) [0] tried to understand the transport and retention of nanoparticles (NPs) in an oilfield environment, such as high salinity, high temperature, high pressure, and heterogeneous pore distribution is critical to their application. They investigated the fundamental transport and retention properties of NPs in the challenging oilfield conditions. They used dolomite and Berea sandstone in flooding operation. The nanomaterial used is Carbon NPs. By comparing the breakthrough time of water and nano material, the results showed that the existence of salt ions dramatically delayed NP breakthrough time and increased NP retention.

Onyekonwu-Ogolo in 2010 [0] used three different polysilicon nanoparticles (PSNP) to EOR by changing the rock wettability. The core rocks obtained from Niger Delta, and three PSNP used; lipophobic and hydrophilic PSNP (LHPN); hydrophobic and lipophilic PSNP (HLPN); and neutrally wet PSNP (NWPN). The wettability change and lowering interfacial tension (IFT) are the main recovery mechanisms using NWPN and HLPN in water wet formations. LHPN which make already water wet rocks strongly water wet yield poor recovery factors indicating that its use for EOR should be restricted to oil wet formations. Table 1 shows the comparative results between all the nano fluid used.

Table 1: Results of recovery efficiency

Core Plug No.	% Recovery Improvement
CN1A	29.73
CN2A	1.59
CN3A	56.88
CN4A	55
CN1B	10.81
CN2B	3.26
CN3B	69.09
CN4B	80.85

Kanj et. al. (2011) [0] presented the first lab plus field trial of nano agents application on the giant oil field at Saudi Arabia, Ghawar field. The formation was Arab-D carbonate rock. Their challenges involve a high temperature reservoir greater than 100 ^{o}C and high connate water salinity about 120,000 ppm (total dissolved solids, TDS). The nano particle used is called A-Dots, they are carbon based fluorescent nanoparticles. Carbon nanoparticles represent a unique class of nanomaterials that are generally synthesized through a hydrothermal treatment process. The recovery factor achieved experimentally using A-Dots nanoparticles is exceeding 96% as depicted in Figure 4.

Field testing of the A-Dots was made in an observation well in a huff and puff mode. The analysis of the fluid samples collected from the well over a period of 2 days confirmed a high cumulative recovery (86%) in nanoparticles despite the fact that the well was shut-in for up to 3 days and the well is at a close proximity (1-3 km) to a line of five power water injectors.

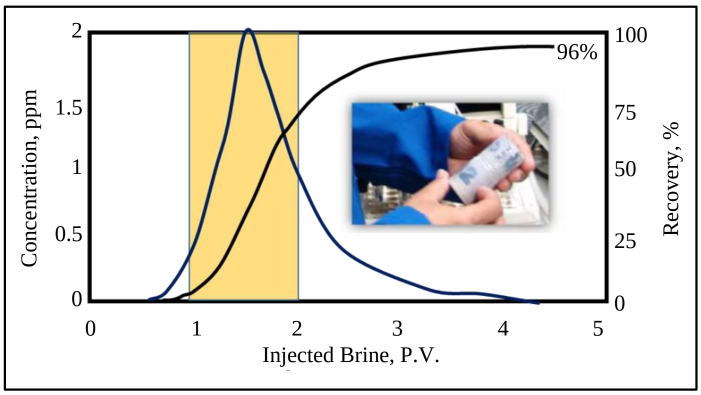

Figure 4: The A-Dots concentration in the effluent and total recovery for carbonate rock core plug.

3. NANO MATERIAL AND CHEMICAL EOR

Qiu-Mamora (2010), [0] studied experimentally the performance of nano-particles and surfactant- stabilized solvent-based emulsion for the heavy oil in Alaska North Slope Area. Berea and Idaho cores were used. In the Berea core flood experiments, emulsion flooding increased the oil recovery factor by 19.2 points after water flooding (from 76.2% to 95.4% OOIP) and the oil recovery with pure emulsion flooding was 96.8% OOIP. In the Idaho core flood, oil recovery increased by 26.4 percent points from 56.2% OOIP with water flooding to 82.6% OOIP with injection of emulsion following water flooding. With pure emulsion flooding, oil recovery is slightly higher at 85.8% OOIP, (Table 2). In conclusion, the nano-emulsion flooding can be an effective enhancement for an oil recovery method for a heavy oil reservoir which is technically sensitive to the thermal recovery method.

Table 2: The results of nano-particle emulsions flooding on Berea and Idaho

Run No.	Core	RF by Wf	Pv Inj. till WF	RG by Emulsion	Pv Inj. after WF
1	Berea	76.2	2.1	95.4	1
2	Berea			96.81	1.6
3	Idaho	56.2	1.2	82.6	1
4	Idaho			85.8	1.4

In 2012, Baez et. al. [0] used amphiphobic nanoparticles based on functionalized carbon nanotubes (CNT) to lower the interfacial tension in EOR. The challenges were to make the CNT-solution stable in presence of brine by using surfactant or polymer and propagating through the porous media and make the required reaction.

In 2012, Miranda et. al. [0] studied the stability and mobility of functionalized (hydroxylated, PEG and sulfonic acid) silica nanoparticles for enhanced oil recovery applications, particularly at high salt concentration and high temperature. The results indicated that adsorption properties and salt solutions greatly influence the interfacial tension. This effect was found to be due to the difference in distribution of ions in solution, which modifies the hydration and electrostatic potential of those ions near the nanoparticle. The brine/oil interfacial tension variation due to functionalized silica nanoparticles was also determined as a function of the terminal group hydrophobicity at 1% salt concentration (CaCl2 and NaCl), 300K and 0.1 MPa pressure.

In April 2012, Ogolo et. al. [0] investigated the performance of eight nano particles namely oxides of Aluminum, Zinc, Magnesium, Iron, Zirconium, Nickel, Tin and Silicon for enhanced oil recovery. These nanoparticles were used to conduct EOR experiments under surface conditions. Distilled water, brine, ethanol and diesel were used as the dispersing media for the nanoparticles. Two sets of experiments were conducted. The first involved displacing the injected oil with the nanofluids. In the second case, the sands were soaked in nanofluids for 60 days before oil was injected into the system and displaced with low salinity brine. Generally, using nanofluids to displace injected oil produced a better result. Results obtained from the experiments indicate that Aluminum oxide and Silicon oxide are good agents for EOR. Aluminum oxide nanoparticle is good for oil recovery when used with distilled water and brine as dispersing agents (see Table 3).

Table 3: Results of oil recovery by injection of various nanofluids into the sands (after SPE 160847)

No.	Nanoparticles	Distilled Water		Brine		Ethanol	
		Total %RF	% RF due to Nano	Total %RF	% RF due to Nano	Total %RF	% RF due to Nano
1	Control Experiment	25	0	35	0	46.7	0
2	Aluminum Oxide (Al2O3)	37.5	12.5	40	5	45.8	-0.9
3	Magnesium Oxide (MgO)	26.7	1.7	32.5	-2.5	42.5	-4.2
4	Iron Oxide (Fe2O3)	34.2	9.2	35	0	42.5	-4.2
5	Nickel Oxide (Ni2O3)	27.5	2	36.7	1.7	41.7	-5
6	Zine Oxide (ZnO)	28.3	3.3	30.8	-4.2	42.5	-4.2
7	Zirconium Oxide (ZrO2)	29.2	4.2	31.7	-3.3	41.7	-5
8	Tin Oxide (SnO)	28.3	3.3	31.7	-3.3	33.3	-13.4
9	Silane treated Silicon Oxide (SiO2)	25.8	0.8	39.2	4.2	51.7	5
10	Hydrophobic Silicon Oxide (SiO2)	x	x	x	x	48.3	1.7

For the use of ethanol, Silane treated Silicon oxide gave the highest recovery in all the conducted experiments while hydrophobic Silicon oxide in ethanol also yielded good results. Aluminium oxide reduces oil viscosity while Silicon oxide changes rock wettability in addition to reduction of interfacial tension between oil and water caused by the presence of ethanol.

For the use of diesel as a nanoparticle dispersing fluid, because diesel and crude oil are miscible, the actual crude oil recovery cannot be determined but the overall result with Aluminium, Nickel and Iron oxides appears good. Magnesium oxide and Zinc oxide dispersed in distilled water and brine cause permeability problems. Generally, distilled water lowers oil recovery.

In June 2012, Mandal et. al. [0] revealed that Nano - emulsions are a class of emulsions with a droplet size in the range of 50–500 nm and have attracted a great deal of attention in recent years because of its unique characteristics. Oil-in-water nano-emulsion which can be formed by high-energy emulsification techniques using specific surfactants can reduce oil-water interfacial tension (IFT) by 3-4 orders of magnitude. They studied the ability of such nano-emulsion to reduce the interfacial tension and understanding the mechanism of mobilization and displacement of entrapped oil blob by lowering interfacial tension both at the macroscopic and microscopic level. They investigated experimentally physicochemical properties and size distribution of the dispersed oil droplet in water phase. Then they carried a flooding experiments in a sand pack system to evaluate the effectiveness of the nano-emulsion as displacing fluid for enhanced oil recovery. Substantial additional recoveries (more than 30% of original oil in place as shown in Figure 5) over conventional water flooding were obtained in the present investigation.

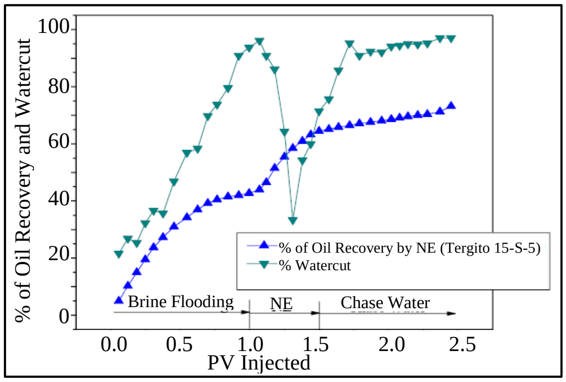

Figure 5: Production performance of Nano-emulsion (NE) flooding for surfactant Tergitol 15-S-5.

3.1 Silica Nano Particles

Silica nanoparticles have been commonly used in EOR projects because of their low-cost fabrication and cost-effective surface modification. Therefore, in 2012, Metin et. al. [0] performed a study for a comprehensive understanding of the rheological behavior of silica nanoparticles. They concluded that the viscosity of nanoparticle dispersions depends strongly on the particle concentration. In addition, during flow in permeable media, the variation of shear associated with complex pore morphology and the interactions between the nanoparticles and tortuous flow channels can affect the viscosity of nanoparticle dispersion.

In 2012, Shahrabadi1 et. al. [0] investigated a special type of polysilicon nanoparticle (HLP, Hydrophobic and Lipophilic Polysilicon) as an EOR agent during different water injection scenarios. The water-wet sandstone core samples are employed. Injection of HLP nanoparticle dispersed in a carrier fluid can improve oil recovery through two mechanisms: reduction of interfacial tension and wettability alteration. Three scenarios of HLP nanofluid injections are applied. First, the nanofluid is injected after waterflooding at ultimate oil saturation. Second, 3 PV water injection is applied after the sequence of water and HLP nanofluid injections. Third, HLP nanofluid is injected from beginning. HLP nanofluid application lowers the oil-water interfacial tension by a factor of ten as well as changing the contact angle from 123° to 99°indicating less water wet condition, i.e. HLP nanofluid alters rock wettability from strongly water-wet to less water-wet state and reduces interfacial tension between oil and water. In all scenarios, the most of oil recovered through the first injected pore volume as shown in Figure 6.

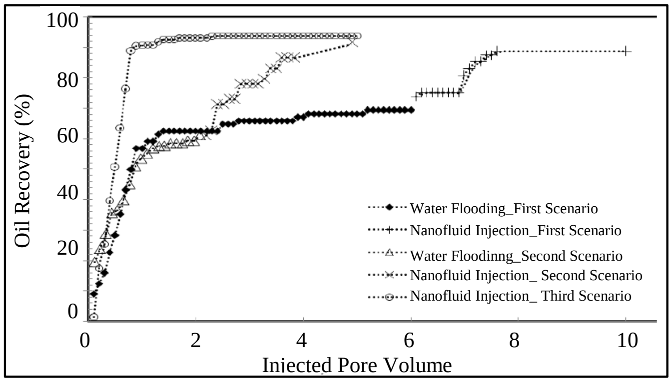

Figure 6: Oil recovery vs. injected pore volume for different scenarios.

In 2012. Roustaei et. al. [[22]] investigated experimentally special type of Nanoparticles named Polysilicon ones which are very promising materials to be used in near future for enhanced oil recovery (see Figure 7). There are three types of Polysilicon Nanoparticles which can be used according the reservoir wettability conditions. They used hydrophobic and lipophilic polysilicon (HLP) and naturally wet polysilicon (NWP) as EOR agents in water-wet sandstone rocks. Both HLP and NWP Nano fluids improve oil recovery through two major mechanisms of interfacial tension reduction and wettability alteration to less water-wet condition. Then concluded also that, NWP Nanoparticles have stronger impact on rock wettability while, HLP Nanoparticles have higher influence on reduction of oil-water interfacial tension.

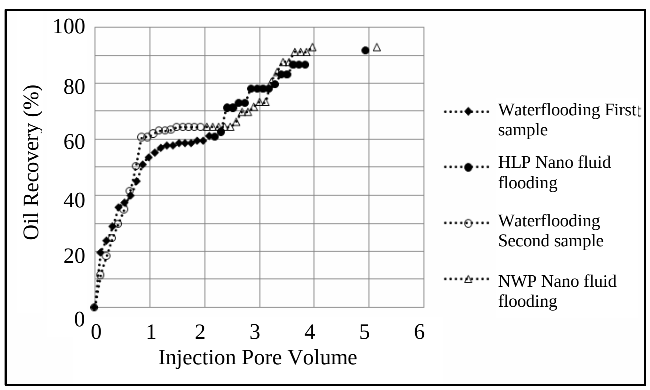

Figure 7: Oil recovery results for waterflooding and nano fluid injection.

In 2012, Nguyen et. al. [0] introduced the synthetic process and the evaluation results for surfactant/polymer inorganic nano- composite specially designed for the enhanced oil recovery (EOR) process in the high temperature and high brine-hardness offshore reservoirs. The results show that the nano composites produced IFT reduction and viscosity enhancement at critical concentration, high thermo-stability and salt-tolerance. These improved properties of core/shell NPs were suitable for producing high sweep volume and increasing crude oil displacement efficiency. The core flooding experiment was performed at 92^o C on the fractured-granite core model and brine blend of 800 ppm of surfactants and 200 ppm of core-shell NPs was injected in 0.25 PV. After water flooding, the oil saturation was reduced into 30% and by the core-shell NPs injection, the oil was displaced in 6.2% additionally.

3.2 Nanomaterial and Improving Relative Perm

In 2012, Parvazdavani et. al. [0] showed that one kind of poly silicon particles with sizes ranging from 10-500 nm, can be used in oilfields to enhance the oil recovery of water injection by 15-20%. The contributing mechanism might be reducing the interfacial tension which appears through improving relative permeability of the oil-phase. The core used in their study was sandstone rock sample saturated by light crude oil supplied from one of Iranian oil reservoir. This work illustrates for the first time the role of dispersed silica particles on hysteretic trend of two-phase oil-water relative permeability curves (see Figure 8).

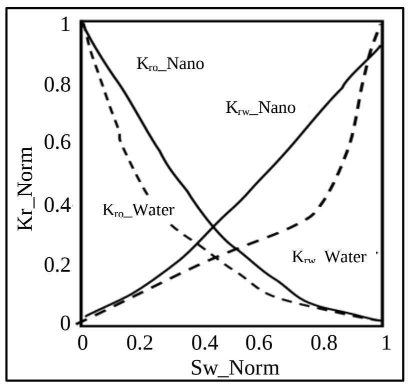

Figure 8: Comparison of relative permeability curves in both cases of water and Nano fluid injection in normalized scale

3.3 Retention and Loss of Nano Material

In April 2012, Yu et. al. [0] indicated that understanding the transport and retention of nanoparticles (14-nm) in porous media is critical to their application. They studied the adsorption and transport behavior of nanosilica particles in three different porous media: sandstone, limestone, and dolomite. The results revealed that the equilibrium (less than 12-hr) adsorption of the particles on sandstone, limestone, and dolomite were 1.272 mg/g, 5.501 mg/g, and 0 mg/g, respectively, in 5,000 ppm nanosilica dispersion. Coreflood tests were performed to investigate nanosilica particles transport behavior in different cores. It was observed that silica nanoparticles could easily pass through the sandstone core without changing the core's permeability. A little adsorption was noted as silica nanoparticles flooded limestone core, but the core permeability was not changed. A high particle recovery was obtained with the dolomite core.

In 2012, Hendraningrat et. al. [0] investigated experimentally the interfacial tension reduction, nanoparticles retention and permeability impairment in porous media by injecting nanoparticles suspension into glass micro model. The deposition and pore-blockage of nanoparticles in glass micro model were investigated (see Table 4) and microscopically visualized by taking sequential images. A hydrophilic nanoparticles and synthetic seawater (brine, NaCl 3 wt. %) as base fluid were chosen in their study. The nanofluids were made with various concentration from 0.1 to 1.0 wt. %. The sonicator as liquid homogenization tool was used just before injecting the nanofluids into glass micro model to avoid agglomeration. Based on microscopic visualization from glass micro model, it observed nanoparticle has deposited and adsorbed at surface pore network.

Table 4: Summary of Dynamic IFT, Nanoparticles (NPs) Entrapment and Permeability Impairment measured at room condition. Some of them were no data due to damage pressure gauge. Dynamic IFT of Brine is 65.41 mN/m

Nanofluids	Dynamic IFT (mN/m) @Equilibrium	Injection rate (cc/min)	NPs entrapped	Permeability Impairment
HNP-A (0.1 wt.%)	51.68	0.1	63.37 %	50.86 %
		0.5	35.16 %	46.90 %
		1.0	22.83 %	45.71 %
HNP-A (0.5 wt.%)	31.03	0.1	39.87 %	No data
		0.5	33.76 %	48.56 %
		1.0	15.76 %	40.98 %
HNP-A (1.0 wt.%)	27.67	0.1	72.57 %	No data
		0.5	50.12 %	68.64 %
		1.0	45.14 %	72.01 %
HNP-B (0.1 wt.%)	39.17	0.1	55.88 %	16.58 %
		0.5	8.82 %	17.76 %
		1.0	10.54 %	20.28 %

3.4 Modeling and Simulation of Nanoparticles

In June 2012, El-Amin et. al. [0] described mathematically the nanoparticles transport carried by a two-phase flow in a porous medium. Both capillary forces as well as Brownian diffusion are considered in the model. A numerical example of countercurrent water-oil imbibition is considered. They monitored the changing of the fluid and solid properties due to the addition of the nanoparticles using numerical experiments. Moreover, they investigated the variation of water saturation, nanoparticles concentration and porosity ratio.

4. CONCLUSIONS

Nanotechnology offers real possibilities of changing the way in which we look at Enhanced Oil Recovery; based on all of these works, the following conclusions can be drawn:

i. Converting the particle size to its nano size cause a great change in some physical, chemical, and biological characteristics, and show different properties than we expect from larger particles of same kind to exhibit.
ii. Several oxides can be used in nano scale to improve the recovery in addition to silicon oxide such as Aluminium oxide, iron oxide, magnesium oxide and zinc oxide, and the stability of the solution after mixing with the nano particles has been discussed.
iii. In upstream applications, most attention is currently devoted to research in development of new nanostructured "smart fluids" for EOR/IOR. The feasibility of mobilizing nanoparticles (< 100 nm) in the reservoir rocks have been demonstrated as in case of "ARAB-D" formation, since, it is proved that the silica nanoparticles can easily pass through the formation without changing its permeability.
iv. The potential of nanotechnology to transform the design and execution of chemical EOR have been addressed. The study provides valuable information for nano materials application for improving oil recovery.
v. Polysilicon nanoparticles (PSNP) after treated with single layers organic compound and silane alter the wettability of the rocks.
vi. The main mechanisms for improving oil recovery using nano materials are Significant reduction of interfacial tension and wettability alteration.
vii. This summary is considered as a roadmap to avoid the ongoing trial and error practice in this area.

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