The Impact of Sparkling Mechanism on Improving Oil Recovery in Nano-Particle Injection through Pseudo-3-Dimensional Micromodels

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Abstract: Nano-materials and nano-particles are used in oilfields to enhance injection processes by changing wettability of porous media, increasing the viscosity of injecting fluid, decreasing the interfacial tension between injection fluid and reservoir fluid. Light alcohol-based nano-fluid slugs (here neutrally wettable nano-silicon) decrease the underriding of injection fluid and improve the vertical sweep efficiency. In addition, small size of nano-particles makes it possible to push the oil in the small pores that remain unrecoverable in polymer injection (named Inaccessible Pore Volumes). Despite of continuous fluid bulks, there is another advantage about dispersed particles; dispersed particles can hit the porous media wall and remove the oil on the wall. This mechanism that is here called "Sparkling Mechanism" significantly improves the oil recovery factor in comparison with the same viscosity polymeric fluid through "Pseudo-3-Dimensional" glass micromodels which are using innovatively in this work.
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1. Introduction

Micro and nano technologies have already contributed significantly to technological advances in a number of industries, including the electronics, biomedical, pharmaceutical, materials and manufacturing, aerospace, photography, and more recently the energy industries. Micro and nano technologies have the potential to introduce revolutionary changes in several areas of the oil and gas industry, such as exploration, drilling, production, enhanced oil recovery, refining and distribution. For example, nanosensors might provide more detailed and accurate information about reservoirs; specially fabricated nanoparticles can be used for scale inhibition; structural nanomaterials could enable the development of petroleum industry equipment that is much lighter and more reliable and long-lasting; and nanomembranes could enhance the gas separation and removal of impurities from oil and gas streams. Other emerging applications of micro and nano technologies in the petroleum industry are new types of “smart fluids” for enhanced oil recovery (EOR) and drilling (Kong and Ohadi, 2010). Nano fluids have attractive properties for applications where heat transfer, drag reduction, formation consolidation, gel formation, wettability alteration, and corrosive control are of interest. Nano fluids can be designed by adding nano-sized particles in low volumetric fractions to a fluid. The nano particles modify the fluid properties, and suspensions of nano-sized particles can provide numerous advantages. Nano-sized particles can impart sedimentary, thermal, optical, mechanical, electrical, rheological, and/or magnetic properties to a base material that can enhance its performance (Singh and Ahmed, 2010). An innovative drag reduction method was put forwarded to decrease the drag of laminar flows of water through rock’s micro-channels and then decrease the injection pressure of flooding significantly. The solution containing hydrophobic nanoparticles of SiO_2 is injected into the micro-channels of reservoir (Di et al., 2010).

Engineered nanoparticles have properties potentially useful for certain oil recovery processes and formation evaluation. Nanoparticles are small enough to pass through pore throats in typical reservoirs, but they nevertheless can be retained by the rock. The ability to predict retention with distance traveled, and to predict the effect of different surface treatments on retention, is essential for developing field applications of such particles (Rodriguez et al., 2009).

Nanoparticles have been speculated as good in-situ agents for solving reservoir engineering problems. Some selected types of nanoparticles that are likely to be used include oxides of Aluminum, Zinc, Magnesium, Iron, Zirconium, Nickel, Tin and Silicon. It is therefore imperative to find out the effect of these nanoparticle oxides on oil recovery since this is the primary objective of the oil industry. 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 (Ogolo et al., 2012).

Nanometer polysilicon materials could change the wettability of porous surfaces. Polysilicon, of which SiO_2 is the main component, is obtained by adding an additive activated by γ -ray to form a kind of modified ultra- fine powder with particle size ranging from 10 to 500 nm. According to their surface wettability, polysilicon particles can be classified into three types: lipophobic and hydrophilic polysilicon (LHP), neutrally wettable polysilicon (NWP) and hydrophobic and lipophilic polysilicon (HLP) (Ju et al., 2006). One kind of polysilicon with sizes ranging from 10~500nm, and considered as nanometer or sub nanometer sized powder, was used in oilfields to enhance water injection by changing wettability of porous media. The mechanism of enhancing water injection is through improving relative permeability of the water-phase by changing wettability induced by adsorption of polysilicon on the porous surface of sandstone. On the other hand, the adsorption on the porous surface and plugging at the small pore throats of the polysilicon may lead to reduction in porosity and absolute permeability (K) of porous media for pore sizes from 100 to 1000,000 nm. Thus the degree of success in well treatment is determined by the improvement of effective permeability of the water-phase (Binshan et al., 2002). 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 (Yu et al., 2012).

Metal Nanoparticles are used for thermal conductivity enhancement of super critical-CO_2 (sc-CO_2) or Viscosity reducing Injectant (VRI) for reducing the viscosity of heavy oil rapidly as compared to conventional sc-CO_2 or VRI. A sc-CO_2 soluble surfactant has also been added to the mixture to further enhance the viscosity reduction. Thus the thermal properties of metal nanoparticles, the chemical properties of surfactant and the miscible properties of sc-CO_2 and VRI altogether reduce the viscosity of heavy oil (Rusheet, 2009).

It has recently been shown that micron-sized metal particles improve the efficiency of some ex-situ processes such as coal liquefaction and pyrolysis, heavy oil upgrading, oil shale recovery, and heavy oil viscosity reduction. This idea, with some modifications, can be applied to reduce the energy input of the aforementioned recovery methods for more economical heavy oil/bitumen production. The major contribution of the metal particles is expected to improve viscosity reduction by reducing the amount of the required energy (Shokrlu and Babadagli, 2010). Paramagnetic nanoparticles have potential applications for enhanced oil recovery (by imposing an external field to control the behavior of injected fluids) and especially for evaluating oil saturations and other properties of an EOR target formation (by imposing a magnetic field near the wellbore after injecting fluid and measuring the response). However, the first requirement for these applications is the ability to place the particles a desired distance from the injection well. This means the particles should exhibit little retention in sedimentary rock and minimal formation damage. The ability to predict and control the degree of retention will be valuable for designing field trials and applications of such particles (Yu et al., 2010).

Single-Walled-Carbon-Nanotube (SWNT)-Silica nanohybrid particles are a very promising material that could be used in a near future for enhanced oil recovery because of their interfacial activity. The mechanism used to recover additional oil in this case would be to deliver catalytically active nanohybrid particles to the oil-water interface, where they would react with and modify the oil properties to mobilize the oil in the reservoir (Villamizar et al., 2010).

Nanoparticle-stabilized emulsions have attracted many researchers' attention in recent years due to many of their specific characteristics and advantages over conventional emulsions stabilized by surfactants or by colloidal particles. For example, the solid nanoparticles can be irreversibly attached to the oil-water interface and form a rigid nanoparticle monolayer on the droplet surfaces, which induce highly stable emulsions. Those emulsions can withstand harsh conditions. Compared to colloidal particles, nanoparticles are one hundred times smaller, and emulsions stabilized by them can travel a long distance (Zhang et al., 2010). Nanoparticles are two orders of magnitude smaller than colloids and thus can migrate through the pore throats in sedimentary rocks. Emulsions stabilized with nanoparticles can withstand the high-temperature reservoir conditions for extended periods. This can substantially expand the range of reservoirs to which EOR can be applied. Finally, nanoparticles can carry additional functionalities such as super-paramagnetism and reaction catalysis. The former could enable transport to be controlled by application of magnetic field. The latter could enable in situ reduction of oil viscosity (Zhang et al., 2009).

Core floods in which a CO_2-analogue fluid (n-octane) displaces brine with and without dispersed nanoparticles were conducted in the work of Aminzadeh et al., (2012); it was found that the floods with nanoparticles cause a greater pressure drop, and a change in flow pattern compared to the floods without. Emulsion formation is inferred by measuring the saturation distribution and pressure drop along the core. The results suggest that nanoparticle stabilized emulsion is formed during a drainage process (at low shear rate condition) which acts to reduce the mobility of the injected fluid. Also novel amphiphobic nanoparticles based on functionalized carbon nanotubes (CNT) have shown promising applications for enhanced oil recovery, by lowering the water/oil interfacial tension upon adsorption or chemical reaction catalyzed by these nanoparticles. Challenges for this novel approach include a) stabilizing aqueous suspensions of the nanoparticles in the presence of brine, b) propagating these suspensions through a porous media, c) conducting reactions at the interface. It is well-known that it is difficult to suspend CNT in liquids since they are amphiphobic. Thus, surfactants or polymers are needed to create stable suspensions (Baez et al., 2012).

In the present study, sol-gel derived nano-silicon (NS) that is produced in an alcoholic media (a particle-based light nano-fluid) has been used. A set of flooding experiments has been done in a pseudo-3-dimensional glass-micromodel that is composed of two 2-dimensional micromodels and in addition some tests have been done a simple structure glass-micromodel to show sparkling mechanism in nano-particles flooding. Some of other advantages of nano-particles were revealed in an experimental manner too.

2. Material and Methods

The investigated fluid in this work is nano-silicon (NS) that is synthesized in laboratory using sol-gel method. The process involves hydrolysis and condensation of metal alkoxides (Si(OR)4) such as tetraethylorthosilicate (TEOS, Si(OC2H5)4) or inorganic salts such as sodium silicate (Na2SiO3) in the presence of a mineral acid (e.g., HCl) or base (e.g., NH3) as catalyst (Hench and West, 1990 and Klabunde et al., 1996 and Stober et al., 1968). A general flow chart for sol-gel process which leads to the production of silica using silicon alkoxides (Si(OR)4) is shown in Figure 1. The average particle size of this nano-material is 30-40 nm.

Oil recovery performance of NS flooding is compared with polyacrylamide (PAM) injection, due to its popularity in EOR processes.

Initially glass micromodels have been saturated with an oil sample of 500 centipoise viscosity and then the oil has been removed with NS or PAM and finally their flood results has been compared.

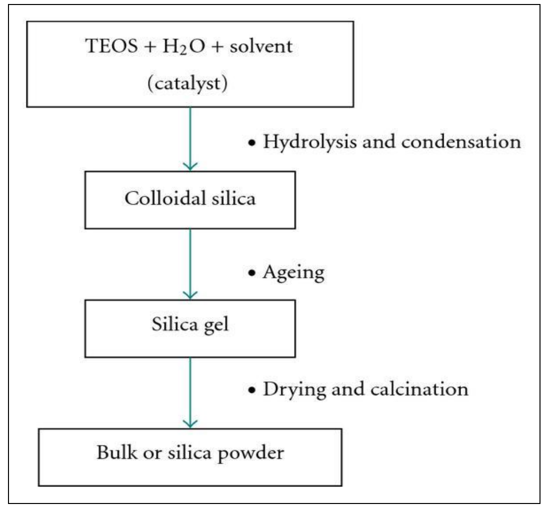

Figure 1. Flow chart of a typical sol-gel process

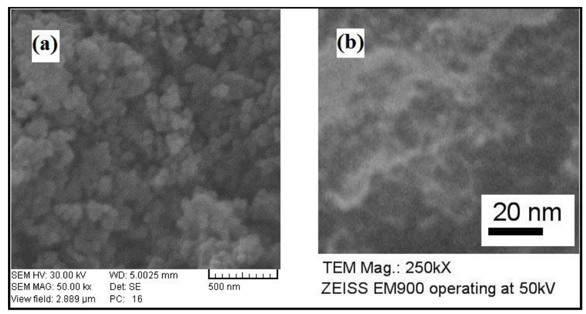

Figure 2. (a): SEM image of NS, (b): TEM image of NS

Better understanding of pore-scale phenomena can be simply achieved by microscopic visualization of the porous media. These patterns were carved onto glass surface using laser etching apparatus. Then a flat plate attached to the carved plate by heating up to 710 ºC gradually and then cooling down in 10 hours to ambient temperature to have a completely sealed glass micromodel. The using patterns of this work are shown in Figures 3, 4, 4 and 5. Simple structure model is a pattern of straight lines and some cavities to investigate inaccessible pore volumes (IPVs) and sparkling mechanism. In Pseudo-3-Dimensional (P3D) model, there are two perpendicular micromodels of dead-end pore structure (for horizontal direction) and vertical-connection (for vertical direction). P3D micromodel is a novel 3D reservoir representative composed of two 2D glass micromodels.

High resolution digital cameras (Nikon D-100, D-90) were used to take photos from micromodels frequently.

A high-accuracy Quizix QL-700 pump was used to inject fluids through micromodels. This pump can inject the fluid in the range of 0.0006 to 10cc/min.

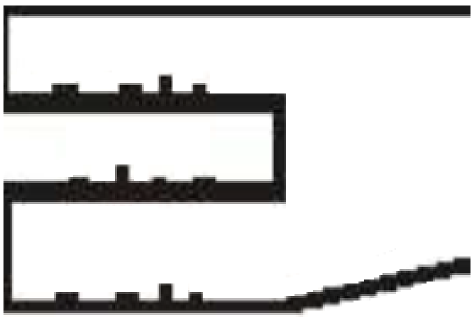

Figure 3. Simple structure micromodel

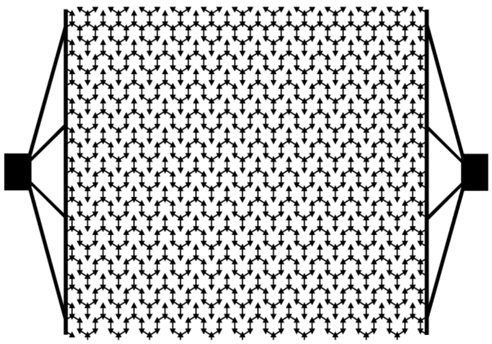

Figure 4. Horizontal plate, containing deadend pores

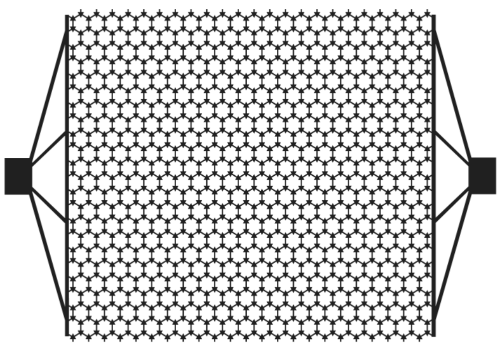

Figure 5. Vertical plate with high vertical connectivity

3. Results

Fluids produced in moderate values of viscosity (3 cp) to have normal ranges of recovery factor (RF), representative of reservoir condition. It is probable to have extra normal recovery factors in high viscosity fluids because of high degree of porous media homogeneity in this set of experiment. Injection rate in all of the flooding tests has been adjusted in 0.001 cc/min.

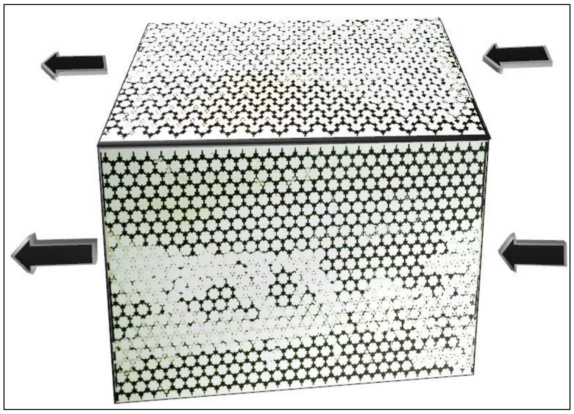

Figure 6. Pseudo-3-dimensional glass micromodel

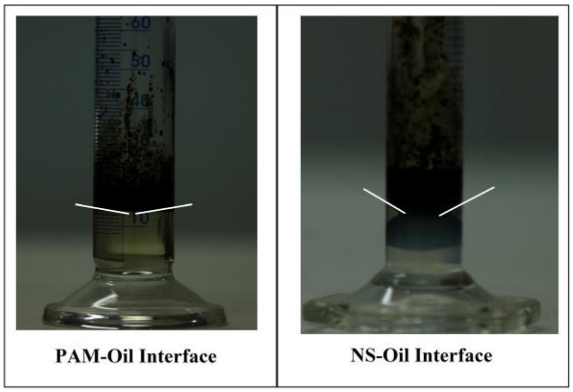

Figure 7. Contact angles of PAM-Oil and NS-Oil systems

After testing an oil-wet (aged) pattern we ensure that NS fluid causes no wettability alteration. As shown in Figure 7 the interfacial tension (IFT) between NS and oil is more than the IFT of PAM-oil system. In simple structure model (Figure 3) because of special structural design, the fluid viscous fingering can be ignored. Thus lower IFT between injecting fluid and reservoir fluid absolutely is a positive parameter in the oil production, so the recovery factor of PAM flooding is expected to be more than the recovery performance of NS flooding, but as shown in Table 1 the recovery factor of NS flooding in this model is more than that for PAM flooding because of sparkling mechanism (particles hit the porous media wall and remove the oil from the wall).

According to the captured photos of micromodels, the oil film on the wall of the porous media remains constant in a few minutes after passing of PAM fluid in a considering point, but the oil film becomes thin with time even several minutes after passing of NS fluid in each point. Considering immiscible fluid contact and lack of fluid diffusion, it is another evidence of sparkling mechanism in NS fluid injection.

Injection of NS fluid after complete PAM injection in the same porous media showing a considerable RF enhancement in spite of PAM fluid injection after NS fluid injection that has no RF enhancement. Considering discussing IFT values, it is a promising evidence of sparkling mechanism in nano-particle flooding of silicon (NS fluid injection).

The density of NS fluid is almost equal to the oil density and relatively less than PAM fluid density. Thus as shown in Table 1, the difference between the recoveries of NS and PAM injections, in vertical side of P3D is much more than horizontal side flooding because of fluid underriding in vertical PAM injection, and it is another advantage of alcohol-based NS fluid in comparison with water-based fluids to be at least frontal slug of injection scenarios.

Table 1. Comparison between PAM and NS recovery factors in different micromodels

		NS	PAM
Recovery Factor Percent	Horizontal Model	35.06	33.88
	Vertical Model	36.39	26.88
	P3D Model*	12.76	9.11
	Simple Model	74.5	73.88

* Multiplication of Horizontal RF and Vertical RF

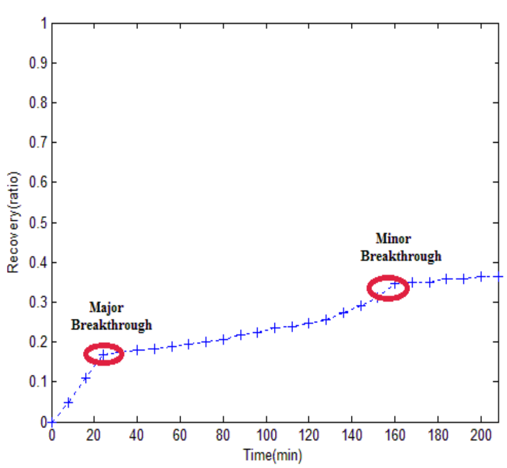

Figure 8. Recovery curve of NS Flooding through vertical side of P3D micromodel

As shown in Figure 8 there are some recovery bumps in vertical-side flooding of P3D model that the slope of recovery curves decreases dramatically after each one of them. Clearly the main part of RF is corresponding to the first part (before the first bump) and of course the main part of the remaining recovery is corresponding to the second section. Image analysis of flooding micromodels shows that the first recovery bump is corresponding to the first branch breakthrough; here called "Major Breakthrough" and second recovery bump is corresponding to the second branch breakthrough; here called "Minor Breakthrough". If there are more than two branches, recovery curves will show more than one minor breakthrough. First recovery period will have maximum recovery quota and subsequently this portion will decrease after each bump, because of pressure discharge of the system and lower pressure depletion along swept area in comparison with unswept area.

4. Discussions

Besides lower IFT between PAM and oil, in comparison with NS-oil system the recovery factor of NS flooding is more than PAM flooding due to the sparkling mechanism. In PAM flooding the oil film on the porous media remains constant but in NS flooding it is reduced because of sparkling mechanism in this system. Sparkling mechanism is more obvious in the injection of NS fluid after complete PAM injection in the same porous media.

The difference between recovery factors of NS and PAM flooding in vertical systems is much more than that for horizontal systems due to lower underriding in vertical NS flooding in comparison with PAM flooding, so NS fluid can be a suitable choice for EOR in large pay zones.

Recovery bumps in vertical flooding case are because of the major and minor breakthrough effects on flood pressure-pattern.

Reservoir 3D model can be easily simulated using P3D micromodels desirably.

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