Alteration wettability of carbonate rocks by Nano fluids and comparison with PEG and SDS

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Abstract:

This work was conducted to study limestone rock wettability alteration to enhance oil recovery by flooding using different Nano silica (NS) sizes suspended in saline water and compared with flooding solution of polyethylene glycol (PEG) polymer and sodium dodecyl sulfate (SDS) surfactant, the stability of nanofluids measured by zeta potential. In the flooding system, the secondary recovery by silica nanofluids (0.01 wt. % NS concentration) achieved an oil recovery of 35vol. % and 26.08 vol. % for 10, 52 nm after primary recovery respectively, while PEG polymer and SDS surfactant achieved oil recovery of 5 vol. % and 10 vol. % only respectively. The stability of pressure difference approved that silica nanoparticle never causes any plug or damage for the carbonate rocks.

تغيير قابلية بلل الصخور الكاربونية بواسطة السوائل النانوية والمقارنة مع البولي اثيلين كلايكول ودوديسيل كبريتات صوديوم

الخلاصة:

البحث يتضمن دراسة تغير قابلية البلل للصخور الكلسية لغرض تعزيز استخلاص النفط عن طريق حقن السوائل النانوية وبأحجام مختلفة من النانو سيليكا (NS) العالقة في المياه المالحة ومقارنتها بعمليات الحقن التقليدية والتي تتضمن حقن البوليمرات كالبولي إيثيلين كلايكوول (PEG) وحقن دوديسيل كبريتات الصوديوم (SDS)، حيث تم دراسة استقرارية المحاليل النانوية من خلال قياس Zeta potential.

من خلال عمليات الحقن، حققت عمليات التعزيز الثانوي باستخدام النانو سيلكا بتركيز (0.01 wt. % NS) زيادة في الانتاج وصلت الى 35 vol. % و26.08 vol. % للحجوم 10, 52 nm بعد الاستخلاص الأولي على التوالي، في حين حقق البوليمر PEG و SDS زيادة في الاستخلاص وصلت الى 5 vol. % و10 vol. % فقط على التوالي. وقد اثبتت استقرارية الضغط على أن الجسيمات النانوية المستخدمة لا تسبب أي ضرر لصخور الكربونات او الكلسية.

Introduction:

One of the major problems faced in the petroleum industry is the depletion of the oil reservoir. After exhaustion of reservoir natural energy, a large part of industry technology was focused on recovering more oil from that remained in the reservoir layer. During the past five decades, EOR (enhanced oil recovery) methods have been progressed and applied to mature and mostly trapped oil reservoirs to increase the efficiency of oil production by retrieving a large part of crude from the reservoirs after primary and secondary recovery processes [1].

Reduction in oil production in carbonate reservoir caused due to reservoir heterogeneity (different permeability zones, channels, and fractures)[2] . Water production due to fingering deep in the reservoir during the sweep process caused due to density and Viscosity differences between injected and natural fluids [4]. Knowledge of the wettability of carbonate reservoir rock is of utmost importance to researchers, where it is fundamental to the understanding of fluid flow through porous media and can affect the production characteristics greatly during water flooding [3].

In Iraq, Mishrif Formation characterized by a high degree of heterogeneity (Porosity of the formation is >22%, and permeability (23 to 775 md). Originally described as organic detrital carbonate with beds of algal, rudist, and coral-reef carbonate, capped by limonitic freshwater limestone[4].

Though the amount of crude oil available has to meet the worldwide demands, crude oil is considered a limited resource which led to serious oil crises accompanied by a general increase in the oil price caused by international reduction of oil production. So, the oil industry was forced to recover oil from complicated areas in which the oil is less attainable, resulting in the development of techniques for enhancing oil recovery (EOR) constantly[5].

Chemical EOR method holds promise for future improvements in oil production, especially in mature and water flooded fields. Chemical EOR classified into a polymer, surfactant, and alkaline agents; in addition, combinations of the three categories such as alkali-polymer, alkali-surfactant polymer, and surfactant-polymer[6]. Chemical injection is qualitative fluid injection which perfectly changes phase conduct properties to increase oil production. Decreasing the interfacial tension of oil /water is the domain of chemical processes. The surfactant used to reduce interfacial tension and polymers are controlled by the mobility of the surfactant solution.

The polymer is used to minimize the relative permeability to water more than to oil. So, the water production controlled without influences on oil production rate. While in sandstone reservoirs polymers injection have been the most applied enhanced oil recovery chemical method [30]. The most important preconditions for using polymer flooding are the formation of water chemical properties and reservoir temperature where the concentration of polymer will lose most of its property at high temperature or /and high saline of formation water in the reservoir, in addition, the polymer cannot be kept stable [7].

Hydrophilic nature of polymer and tendency to flow through the pore wall this makes fingerings during the polymer flooding in an oil-wet medium [8].

Many researchers have attracted attention in Nanoparticles material application in the EOR field because of their capability to change the wettability of the carbonate rock and its ability to decrease the IFT between oil and injection water. Furthermore, increasing the mobility of the trapped oi [9].

Nano-particles has the ability to travel easily through a reservoir; push the residual crude oil in the small pores that unrecovered in polymer injection. Despite continuous fluid bulks, dispersed particles can hit the porous media wall and remove the oil on the wall. Due to NPs small size, they do not aggregate, agglomerate to larger structures or adsorb onto the rock surface compared with reservoir channel that in micrometers size [10].

Experiment Work:

The experiments of this research were carried out at the laboratories of the petroleum research and development center. The chemicals and the analytical test instruments are shown in Table1 and Table (2) respectively.

Table (1) Chemicals and materials specification

Materials and Chemicals	Source and/or company	specification
Carbonate Rock	mishrif formation	$CaCO_3$ 70%.
Sand	Al-Anbar / Iraq	99% silica oxide.
Gas oil	AL-Dura refinery	its density at 15°C was $0.825 g/cm^3$, and kinematic viscosity 4.05cst at 40°C.
Crude oil	PRDC (petroleum research and development center) API 38	Density 0.84 g/cm^3, kinematic viscosity 1.75cst at 40°C.
Nano silica	Sigma Aldrich.	size (5-15nm) and purity 99.99%
Sodium dodecyl sulfate	Himedia Company,	purity 98%
Polyethylene glycol	*Fisher Scientific.*	average Mn 20, 000, Ω-end OH

Table (2) Instruments of analytical tests

instruments	location	
zeta potential analyzer	Ministry of science and technology.	Zeta plus Brookhaven Corporation/USA
Accelerated Surface Area and Porosimetry System	PRDC	ASAP 2020 V3.04 G/ USA
AtomicForce Microscope (AFM)	Baghdad university / college of science	89/USA
Ph meter HANNA	PRDC	H2550/USA
of Benchtop Permeability System (BPS-805)	PRDC	(BPS-805)/USA

Preparation of Nano silica and Nano fluid:

The Nano silica was prepared from Iraqi local sand according to the procedure of previous work [11]. The average particle size and surface area of prepared silica were 52 nm and 474.9429 m^2/g respectively. Nanofluid prepared in two steps. First, a certain amount of Nano silica added to achieve 0.01 wt. % to a base fluid prepared according to the Iraqi reservoir injection water specification as shown in Table 3 and kept under stirring. Second, suspended silica was subjected to sonication using an ultrasonic mixer for 15 min at high energy to avoid agglomeration of particles.

Table (3) Injection water quality

Oil content	30 mg/l
Size of suspended solid	4-10µm
suspended solid	30 mg/l
pH	6.5
TSS	<2

Polymer and surfactant solutions:

Polyethylene glycol and sodium dodecyl sulfate (SDS) solutions were prepared by dissolving under mixing condition in the same base fluid above to obtain a solution concentration from (0.01 wt. %) for polymer and respectively. The same procedure repeated for surfactant with concentration 0.01wt. %

Core flooding process:

Five of medium permeable core samples used with properties shown in Table (4). The samples weighted and saturated with crude oil using vacuum saturation setup. The samples were aged and weighted at various times until the weight became constant.

Table (4) Core samples properties

properties core sample code	Dimension (cm) (length × diameter)	Dry weight (g)	Pore volume (cm^3)	Permeability (mD)	porosity
10nm	3.64*3.7984.57	84.57	41	98	0.248
52nm	3.65*3.78	83.41	40.9	140	0.24
Saline water	3.65*3.79	80.84	41.309	71	0.27
SDS	3.617*3.79	85.08	40.8	211	0.234
PEG	3.631*3.8	79.65	58.9	220	0.293

Benchtop Permeability System (BPS-805) equipment shown in Figure (1) in petroleum research and development center PRDC that used for the core flooding. This piece of machinery can be used to study in a core flood oil recovery in a core sample.

Fig. (1) Benchtop Permeability System (Bps-805) Equipment

Loading sample and operation procedures were done for all prepared fluids (Nano fluids (10, 52nm), modified Nano fluid, PEG fluid, and SDS fluid) according to schematic diagram (2).

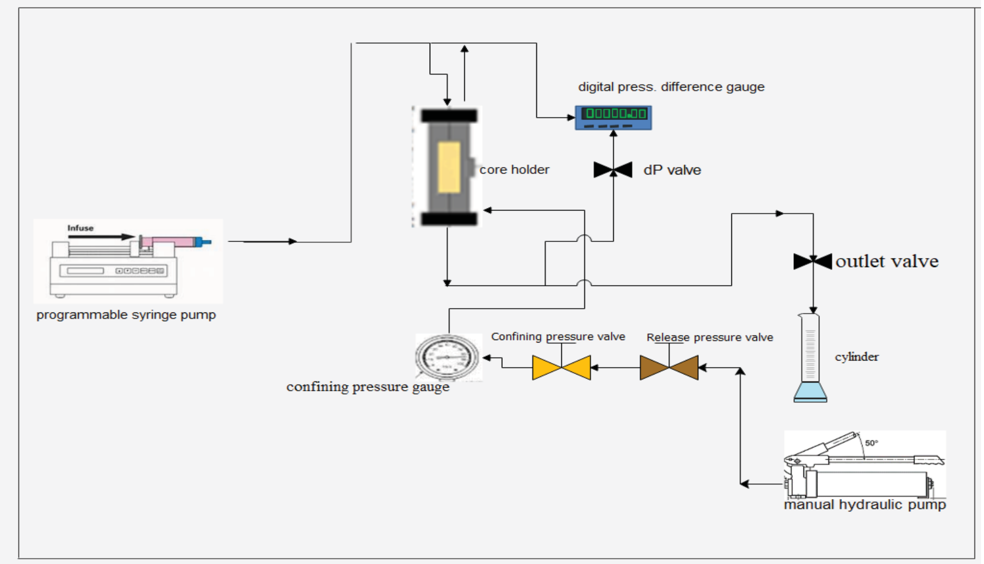


Fig. (2) Scheme of Flooding Process

Operation procedure:

Saline water (30cm^3) injected with flow rate 0.5ml/min as primary recovery. The pressure difference, injection pore volume, and water-oil recovered recorded with time for each run. Then, the prepared nanofluid (30cm^3) injected as a secondary recovery at the same operating procedure of saline water. At the end of the run, distilled water was injected to clean pipes and core holder to prepare for the second run.

Result and Discussion:

Stability of Nano fluid

The stability of Nanofluids was considered by measuring zeta potential. Figures (3-5) showed that the zeta potential values of NPs varied from -137.04, -137.32 and -141.8mV for 65nm, 52nm, 10nm respectively at pH 6.5. The high negative zeta potential value of NPs is attributed to the presence of deprotonated silanol molecules on the NPs surface furthermore high viscosity of fluid due to the presence of oil content.

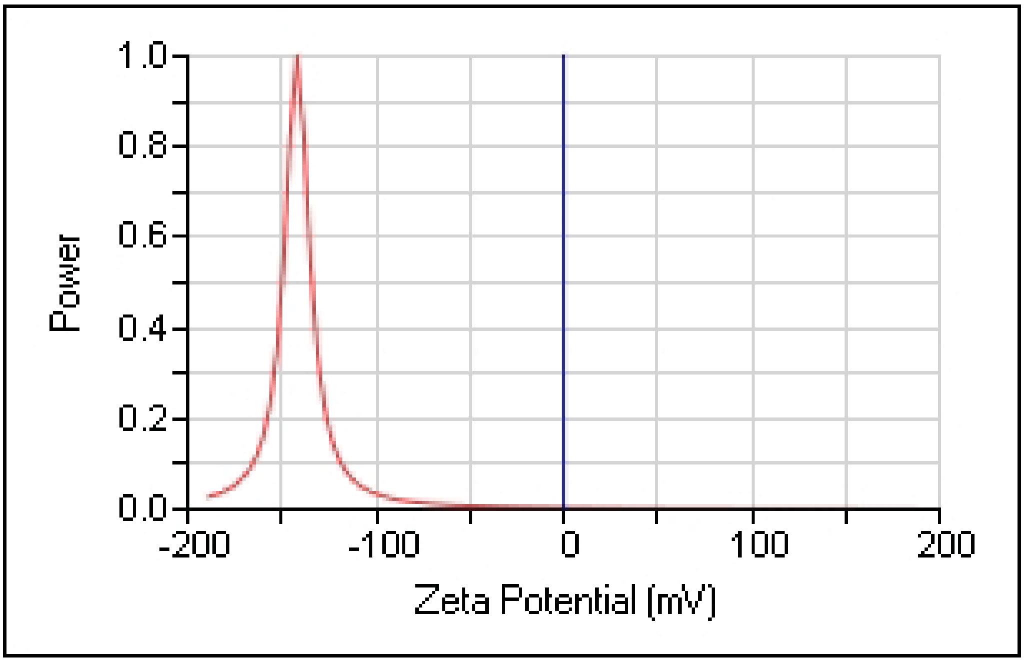


Fig. (3) Zeta potential for Nano fluid of NP size 10nm

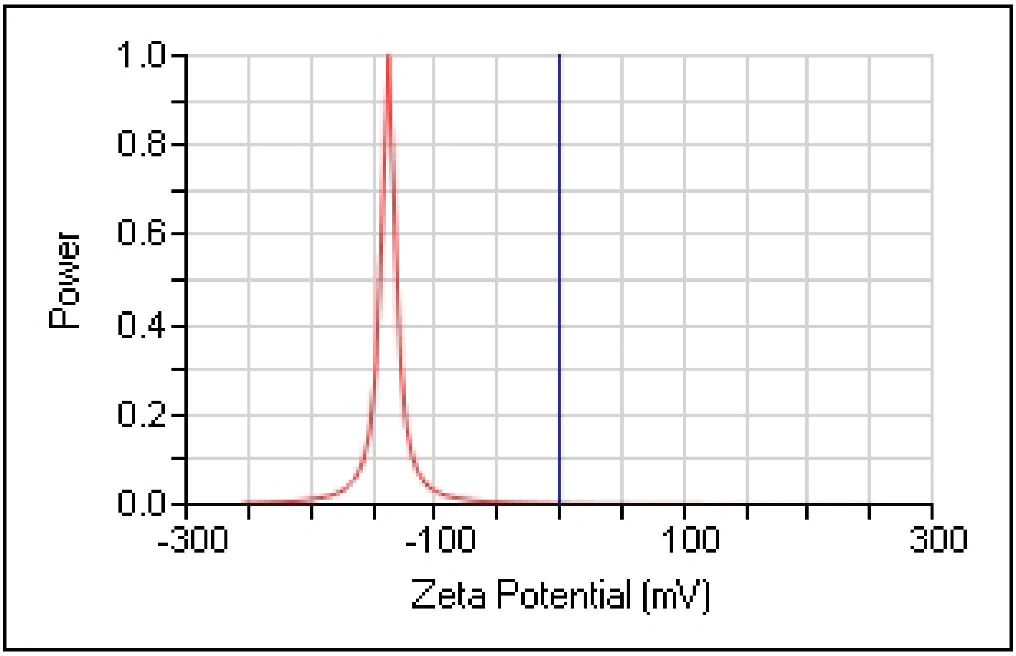


Fig. (4) Zeta potential for Nano fluid of NP size 52nm

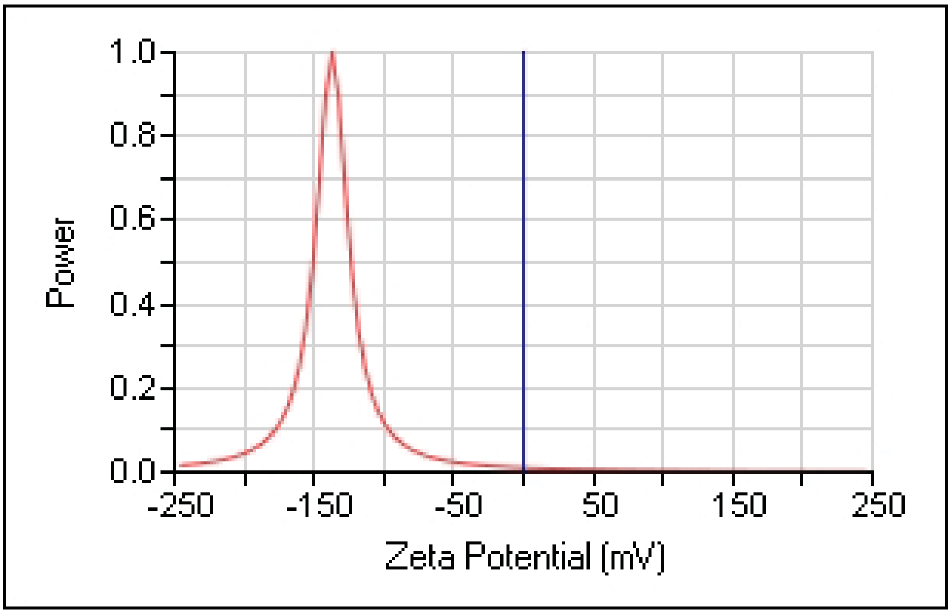


Fig. (5) Zeta potential for Nano fluid of NP size 65nm

Oil Recovery:

Nano fluid injection

A comparison between the recovery results in Figure (6) revealed that Nanofluid could increase an oil recovery after primary recovery processes to (35, and 26vol. %) for particles size 10, 52nm respectively, where the secondary injection submitted when the oil production during primary injection reached breakthrough point and the oil production stopped due to saline water cannot push more oil from small pores . This difference in recovery is due to the difference in surface area. High surface to volume ratio with high contact area enables a high diffusion rate, a mass transfer which can enhance the properties of the fluid [12].

The increase in incremental oil recovery with the decrease in particle size is in accordance with the adsorption of NPs that takes place because of the size of the particles could reduce the pressure through permeability reduction. Also, particles size could impact on dispersion ability, adsorption affinity, and catalytic activity of nanoparticles inside the medium [13].

Nano silica can change the wettability condition to water-wet and improves the oil recovery because one of the important mechanisms that have an effect on the oil recovery is wettability of the medium. In addition, reduction in the interfacial tension makes it easier for oil droplets to move through pore throats by decreasing the work of deformation needed. A higher capillary number causes an increase in oil displacement efficiency. Furthermore, Nanofluid viscosity is higher than water. Therefore, the mobility of the injected fluid decreases and the sweep efficiency improves. [8].

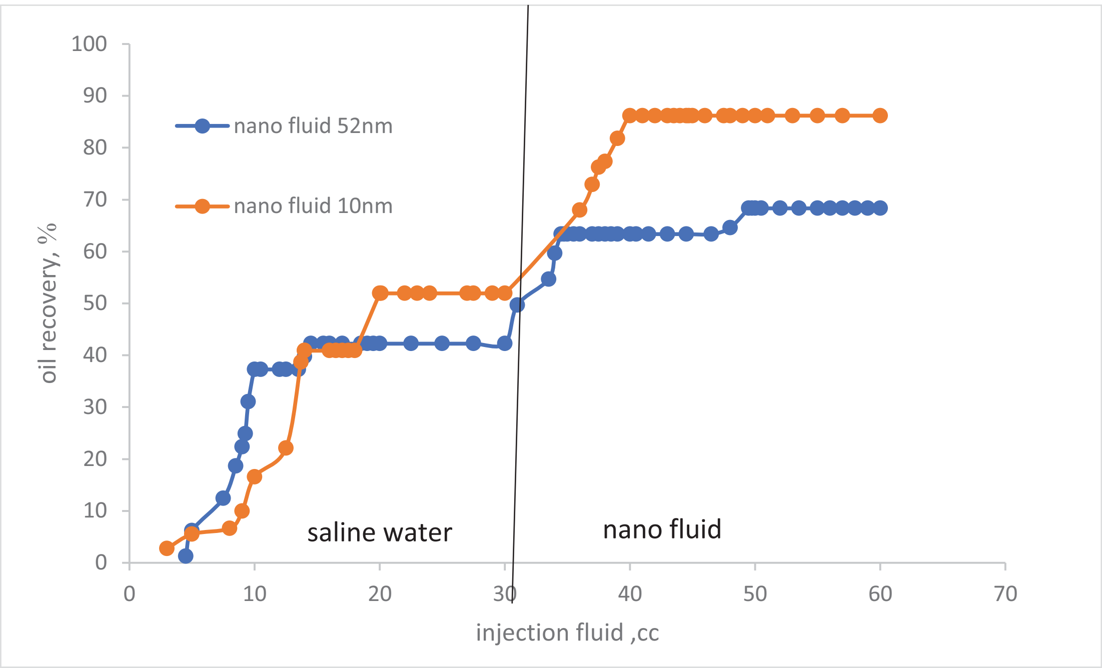
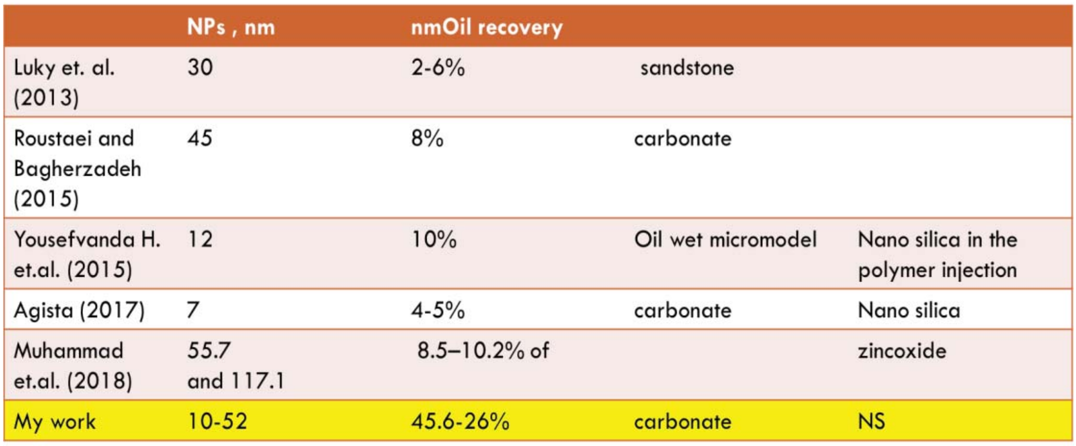


Fig. (6) Oil Recovery Versus Injected Nano Fluid for Different Size of NPS

A comparison of results in the recent research was established with previous work. Where Table (5) showed that the oil recovery of recent research was more sufficient than other studies.

Table (5) Compassion with Previous work



	NPs , nm	nmOil recovery		
Luky et. al. (2013)	30	2-6%	sandstone	
Roustaei and Bagherzadeh (2015)	45	8%	carbonate	
Yousefvanda H. et.al. (2015)	12	10%	Oil wet micromodel	Nano silica in the polymer injection
Agista (2017)	7	4-5%	carbonate	Nano silica
Muhammad et.al. (2018)	55.7 and 117.1	8.5–10.2% of		zincoxide
My work	10-52	45.6-26%	carbonate	NS

Polyethylene glycol injection:

Figure (7) shows that oil recovery increased 5% after primary recovery when the polymer solution with 0.01wt. % injected. Polymer retention decreased to a critical value that reduces an absolute permeability due to high saline water. As the salt concentration increases, charge shielding takes place due to positively charged ions of the salt (Na+), thus the hydrodynamic radius sweep efficiency can be increased of polymer molecule reduces. Due to this intermolecular interaction, electrostatic repulsion in the polymer solution decreases. On another hand, enhance oil recovery to 19.21% and 21.00 vol.% by most common polymer (HPAM) in EOR by Increasing viscosity, it needs to 2000 ppm and 2500 ppm [14].

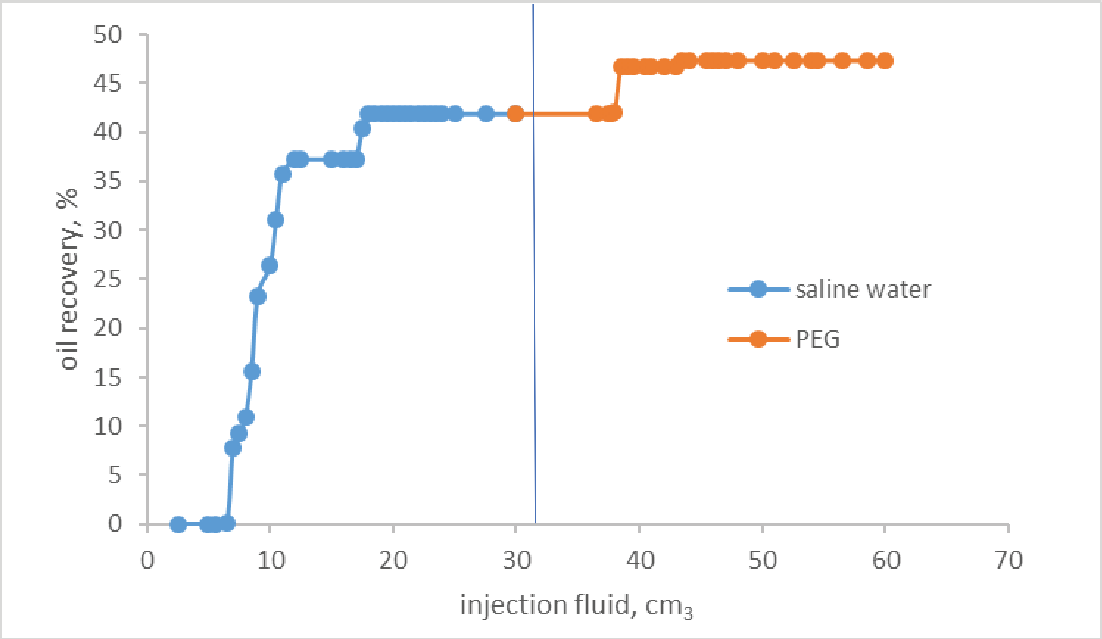


Fig. (7) Oil Recovery Versus Injected Fluid Volume of PEG

Sodium dodycle sulfate injection:

Oil recovery flooding of surfactant SDS increased to 9% above primary recovery as shown in Figure (8). Due to the formation of microemulsions which adsorbed and made phase partitioning inside the reservoir as a result of SDS flooding in which may plug the pores and lose a high percentage of surfactant [5].

Furthermore, surfactant sensitivity to high temperatures and high saline or high concentrations of divalent ions such as dissolved Ca^{+2} or Mg^{+2}. Makes them, surfactants break down, and becoming ineffective. In addition, fractures and natural heterogeneity offer additional complexity to the process[15].

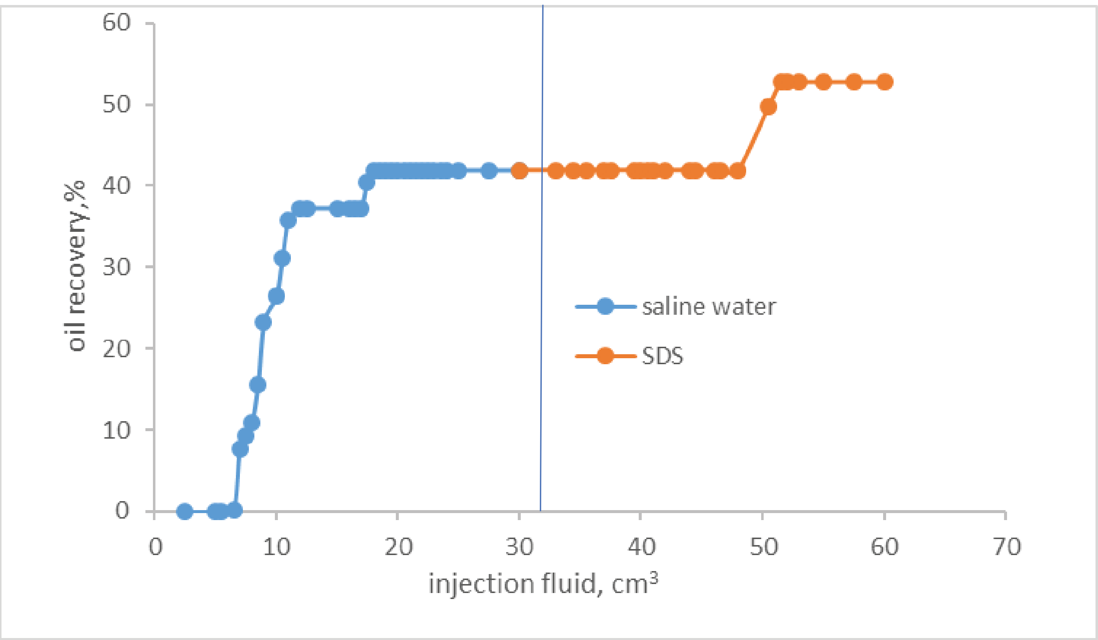


Fig. (8) Oil Recovery Versus Injected Fluid Volume of SDS

Pressure difference:

Recorded pressure drops during flooding experiments are shown in Figures (9) that breakthrough for saline injection, 0.64, 0.74, 0.5, and 0.47 psi for samples SNPs52, SNPs10, PEG, and SDS respectively this difference in pressure drop as a result of different properties of samples. During water flooding in all core samples, the pressure difference between two ends of the core increases up to breakthrough due to stabilizing of injection rate and displacement of oil by water. This increased pressure drop could be attributed to the migration of fines. Afterward, graphs remain steady because only water passes through porous media. The general trend for the pressure drop variation in the chalk rock is that as the salinity of water decreases, pressure drop across the core plug also decreases, due to decreasing viscosity of the saline water)[16].

In all samples, when Nanofluid injection begins, at the first place, a pressure shock observed at 0.69, 0.82, 0.75, and 0.54 psi for, SNPs52, SNPs10, PEG, and SDS respectively due to displacing fluid. However, the pressure drop curve shows different behavior for the injection of different Nanofluids, polymer, and surfactant. After injection of three pore volumes of

Nano-fluid pressure drop raised dramatically due to adsorption of Nano silica into the surface of the rock. According to recovery and pressure drop data, injection of 3 PV of Nano-fluid improves oil recovery without inducing any significant formation damage.

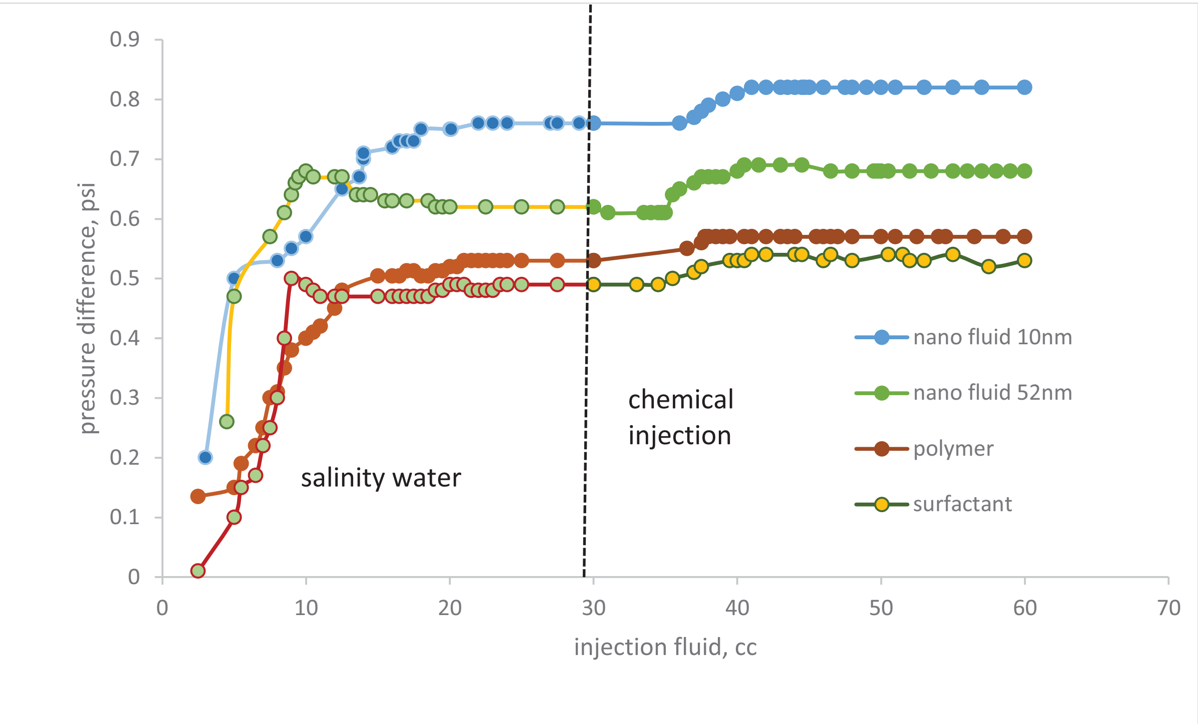


Fig. (9) Pressure Difference Versus Injected Fluid Volume for Different Fluid for Two Step Injection

Conclusions:

Nano silica shows good stability in saline water that simulated to injection water of Iraqi reservoir. Core flood experiments reveal that Nano silica is good EOR agent and can produce a significant amount of oil above primary process 35vol. % and 26.08 vol. % for 10, 52nm Nano silica size respectively. While PEG polymer and SDS surfactant achieved oil recovery of 5 vol. % and 10 vol. % only respectively. The results of the pressure drop across the core sample show no plug or damage observed. This type of Nanoparticles has higher stability under dynamic condition, a low concentrations (0.01wt. %) of Nano silica fluids show a high ability to increase oil recovery from limestone cores through flooding system more than SDS and PEG in the same concentration.

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