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# The effect of smart water and silica nanoparticles injection on wettability of limestone

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**ABSTRACT:** Today, by using half of the oil reserves of the world, natural production of oil has decreased drastically. Gas and water injection for maintaining reservoir pressure is not responsive for oil production. At first, we dispersed silica nanoparticles in low salinity and after two weeks, there was no change in its stability. Then we mixed the nanoparticles in low salinity. After a while, we found out that nanoparticles are completely dispersed but they have lost stability over time. We added silica nanoparticles with different concentrations (0.1, 0.25, 0.5, 0.75, 1, 2) to change the wettability of silica levels of oil-wet to water-wet and observed that at low concentrations silica nanoparticles do not have much effect but it has been effective in concentrations 0.75 to 1 and in concentrations 1 to 2 it has not had much effect. At last, we found that the reason for this is a force called structural disjointing pressure. After diluting, we added salt waters to oil-wet to reduce wettability and we saw that low salinity has destabilized the disjointing pressure of oil films, it tears them, and it replaces films and result in silica surface water-wet. Finally, the tests showed that the use of silica nanoparticles in high concentrations is highly effective and 20-time low salinity are accountable in low concentrations, high temperatures but combining these two solutions increases their effectiveness, and even at ambient temperatures and low concentrations of silica nanoparticles, we see acceptable oil production.

**Keywords:** *Enhanced oil recovery; Low salinity; Silica nano-fluid; Smart water; Wettability*

## INTRODUCTION

Today, after years of oil production in oil fields, natural oil production has dropped and to produce more oil, it is necessary to use second recovery methods. In this method, the goal is to maintain reservoir pressure, which involves injecting water and gas. Again because of reservoir wettability conditions, also reservoir mineralogy complexity, and pore size distribution, oil stays in reservoir and is not produced while injecting gas and water has reached productive well. Therefore, to produce more oil we require fluids that are different from the materials inside reservoir based on chemical and physical combinations. This difference disrupts the geo-chemical and thermodynamic equilibrium and hence it affects the movement and distribution of reservoir fluids. This is tertiary procedure or enhanced oil

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recovery. According to the proposed descriptions, it is necessary to focus on materials that have high efficiency and low cost. To build smart water, seawater is used where in the first approach we add fresh water to seawater for diluting. This method is applicable both in sandstone and carbonate reservoirs. In the second approach by adjusting the chemistry of seawater and adding effective ions on surface potential and removing ineffective ions, they change the wettability of carbonate reservoirs and thus smart water with lower cost will cause oil production. On the other hand, new methods have been used for oil production in which one of these methods is the use of nanofluids. These materials have many specific features such that they can change the rheological fluid mass or by covering the surface of the rocks change its wettability and enhance its strength in specific areas. In addition, if there are surfactants in the environment, they are very sensitive to these substances and increase the activities of them because in oil we have surfactants that can affect the activity of these materials and reduce the tension between injected oil and fluid surface. Ogolo, *et al.* did their research on injecting metal nanoparticles and its impact on enhanced oil recovery. In their experiments, they observed that nanoparticles of aluminum oxide cause a decrease in oil viscosity. In addition, silicon dioxide nanoparticles alter the wettability and thus result in enhanced oil recovery (Ogolo, *et al.*, 2012). Karimi, *et al.* tested the impact of zirconium oxide nanofluids on wettability of carbonate rocks. Finally, they showed that the designed nanofluids could change rock wettability drastically from highly water-wet to highly oil-wet (Karimi, *et al.*, 2012). Hendraningrat, *et al.* injected typical salt water into the core. Then they mixed silica nanoparticles in artificial salt water, created a nanofluid, and injected into the saturated core with oil and after that they found out that injected fluid with silica nanoparticles because of having these nanoparticles, has increased oil recovery to typical injected water salt up to 8% (Hendraningrat, *et al.*, 2012).

Roustayi, *et al.* examined three types of polysilicon nanoparticles (water-wet, hydrophobic and neutral) by injecting and after comparing the results they found that these nanoparticles have resulted in a decrease between the tension of water surface and injected oil from 23.3 mN/m to about 1.75 mN/m and have increased oil production (Roustayi, *et al.*, 2012). Heidarian, *et al.* also examined the effect of nanoparticles on enhanced oil recovery with a new method that in general according to the conducted tests silica nanofluids and water with ignition mechanism can be useful for enhanced oil recovery (Heidarian, *et al.*, 2012). Nejati nejad, *et al.* offered a numerical model for nanoparticles movement and its impact on enhanced oil recovery and found that with an optimized numerical model, it is possible to measure subsidence of nanoparticles in porous media (Nejati nejad, *et al.*, 2013). Maghzi, *et al.* investigated microscopic and macroscopic efficiency of heavy oil recovery in five-spot micromodel porous media in the process of injecting two types of anionic and cationic surfactant and water-based surfactants containing silica nanoparticles and found that silica nanoparticles change wettability from oil-wet to water-wet. As a result, water-based fluid injection containing silica nanoparticles increases recovery (Maghzi, *et al.*, 2013).

Li, *et al.* examined silica nanofluids and salt-water injection and found that the amount of uptake with nanofluid injection increases due to reduced interfacial tension but deposition of nanoparticles have to be considered (Li, *et al.*, 2013). Seyed Mohammadi, *et al.* investigated the effect of gamma-aluminum nanoparticles on wettability of carbonate rocks and by continuing the flooding tests for the third time they found that aluminum nanofluids injection in a 0.5% wt has resulted an approximately 11 % increase in oil recovery (Seyed Mohammadi, *et al.*, 2014). Yousefvand and Jafari, examined enhanced oil recovery in the presence of polymer and nano silica and found that enhanced oil recovery in the presence of materials have increased about 10 %. (Yousefvand and Jafari, 2015). Alomair, *et al.* examined various nanoparticles to provide proper nanofluids for enhanced recovery and consequently they found that silica oxide due to having the highest surface area of nanoparticles, has the largest reduction in interfacial tension and by increasing the percentage of nanoparticles, the interfacial tension is reduced to a greater extent (Alomair, *et al.*, 2015). Hendraningrat and Torsaeter, did their studies on solutions stability in metallic nanoparticles, examined the amount of oil recovery after nanoparticles injection, and found that nanofluids containing nanoparticles of silica are more stable than other oxides and they are highly efficient in enhanced recovery (Hendraningrat and Torsaeter, 2015). Barkhordari, *et al.* examined silica nanoparticles for enhanced oil recovery with specific weights 11.5 and 22 in micromodel with triangular cavities and found that nanosilica injection to saturation pattern of heavy oil is more efficient than its injection to light oil and in heavy oil and light oil enhanced recovery increased 11% and 4% respectively (Barkhordari, *et al.*, 2015). Jafari Berenji, *et al.* investigated the effects of clay minerals in enhanced oil recovery salt water flooding and found that salt water flooding in porous media makes pores interconnected and this will results in the entrapment of oil and sharp rise in intermediate speed in some of the pores and finally and full cleaning of pore track and consequently enhanced oil recovery (Jafari Berenji, *et al.*, 2016). Mahmoody, *et al.* examined the effect of nanosilica flooding and surfactant in high salinity on enhanced heavy oil recovery and found that simultaneous injection of nanoparticles and surfactant increases amount of oil recovery compared with salt-water injection, nanoparticles and surfactant 33, 25.5 and 24.7 percent respectively (Mahmoody, *et al.*, 2016).

In this study, we have tried to investigate the effect of smart water, silica nanofluid and their combination on wettability properties of silica surfaces.

## EXPERIMENTAL ACTIVITIES

### *Materials testing*

In this study, Nowruz oilfield with API = 33 has been used. In addition, hexamethyldisilazane solution for making silica oil-wet, toluene, and methanol for cleaning silica have used. In Table 1 used materials are mentioned.

### *Test method: determination of the interfacial*

Experiments involve preparing a diluted salt water solution and nanosuspensions, oil-wetting the surface of silica, determination of interfacial tension, stability test of nanoparticles in suspension solution, measuring the contact angle between oil and distilled water in different levels which will be explained in the following.

#### *a) Measuring the contact angle*

First 1.5 in 1.5 square-shaped glasses are provided and then they are put in toluene solution for 24 hours to remove any sort of excessive fat. Then the initial contact angle of water-wet is taken and after ensuring of glasses water-wet we oil-wet toluene in hexamethyldisilazane. Then we put glasses inside the oil and after that, we put glasses into the oven to dry. Then, we take its contact angle to ensure it is oil-wet. After that inside solutions and reformer nanosuspensions, we put wettability made of diluted salt water

Table 1. Shows the materials used in the experiment

| Chemical Formula | Molecular Weight | Materials |
|---|---|---|
| $NaCl$ | 58.44 | Sodium Chloride |
| $KCl$ | 74.551 | Potassium Chloride |
| $NaHCO_3$ | 84.007 | Bicarbonate Sodium |
| $MgCl_2.6H_2O$ | 203.31 | Magnesium Chloride+6Water |
| $CaCl_2$ | 110.99 | Calcium Chloride |
| $Na_2SO_4$ | 142.04 | Sodium Sulfate |
| $NaOH$ | 40 | Sodium Hydroxide |
| $SiO_2$ | 60.08 | Nano Silica |
| $C_6H_5CH_3$ | 92.14 | Toluene |
| $CH_4O$ | 32.04 | Methanol |
| $C_6H_{18}Si_2$ | 146.37 | Hexamethyle Disilazane |
| $H_2O$ | 18 | Distilled Water |

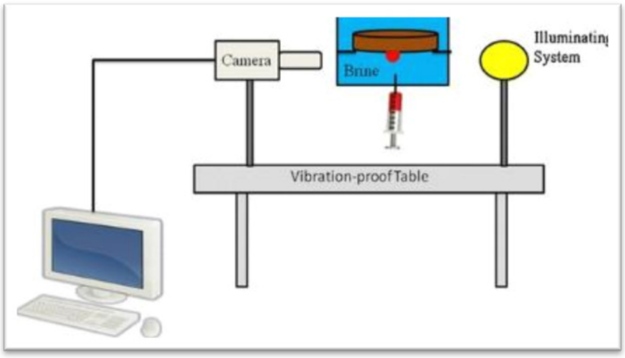


Fig. 1. Schematic measurement of contact angle by sessile drop method

and nanoparticles so wettability of glass get close to its original state and tend to water-wet. Contact angle measurement has been conducted by sessile drop method.

For this purpose, with the help of oil phase, related device (heptane drop) is injected into the cells containing water phase (distilled water) and the oil drop is released. Available microscope and camera system record oil drop image sticking on the surface of glass in three different modes of initial, original and modified wettability and send it to the software. By using MATLAB code of image, analysis drops are analyzed and drops contact angle on tablets surface are obtained in the presence of distilled water. Fig. 1 shows a schematic of this process.

***b) Stability Testes Injected Fluids***

For qualitative evaluation of injected fluids stability photos taken in different times were studied and the number of hours and days that nanosuspensions remained stable were recorded.

## RESULTS AND DISSCUTION

***Examining the stability of silica nanoparticles in different fluids***

Silica nanoparticles with different concentrations have been scattered in 20 time's diluted seawater and based on the figure when the concentration of silica nanoparticles increases, its stability has decreased and becomes unstable after 4 days. Fig. 2 shows silica nanoparticles combinations with different concentrations in 20 times diluted seawater.

Fig. 2. Nanoparticles combinations with different concentrations in 20 times diluted seawater

***Examining different concentrations effect of silica nanoparticles on silica surfaces wettability***

In these experiments, we tested nanoparticles concentration from low to moderate concentrations on wettability change of oil-wet surfaces for 3 days in ambient temperature. As it is clear in the diagram low concentrations does not have a significant effect on wettability change of silica surfaces and they can be seen as a sudden change from 0.75 to 1 % wt and silica surfaces tend to water-wet and when the concentration increases from 1 % to 2%, they do not have much difference in wettability change with each other. Now this is the question: what is the mechanism behind this change? Why we cannot see a significant change in concentration up to 0.75 wt but after that, a sudden change happens? In the previous studies, it has been mentioned that silica or rock surface coating with nanoparticles wettability is the reason for why in this experiment by increasing concentration to 0.75 wt this does not happen. Therefore, it is not possible to say only by sticking nanoparticles on silica surface, wettability change happens. But also there is another mechanism in this regard which causes wettability change and for this change this force must overcome initial wettability while in concentrations lower than 1 % this force was not present. The mechanism that can be mentioned for this is structure disjointing pressure. In this mechanism nanoparticles penetrate around formed oil drops on silica surface because the nanoparticles themselves have a negative surface charge and also negative surface charge of oil and water creates repulsion between these surfaces and nanoparticles with this repulsion remove oil drops from the surface and make the surface water-wet. Wettability change with nanosilica percents are shown in Fig. 3 and diagram 1.

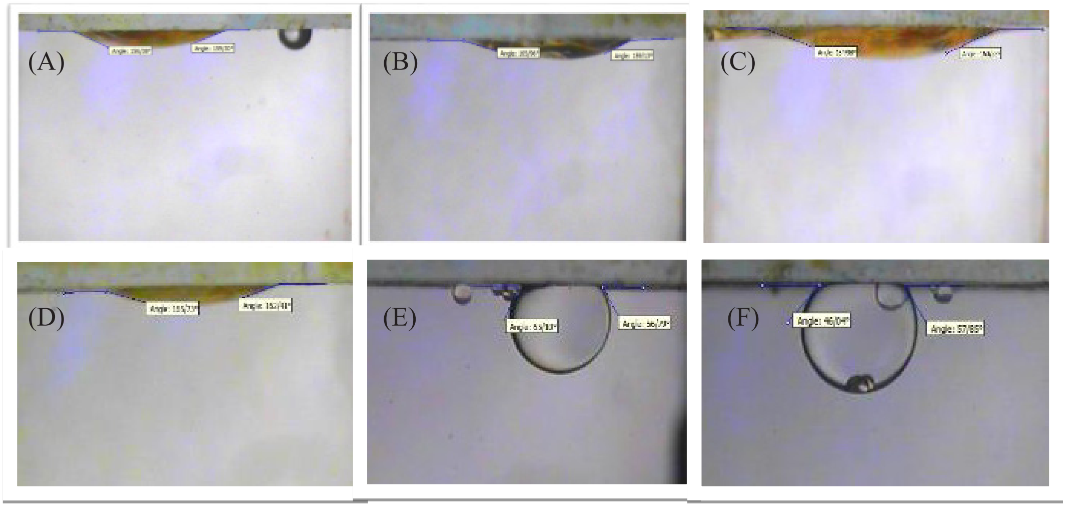


Fig. 3. A - 0.1 wt% of nano-silica , - B - 0.25 wt% of nano-silica , C - 0.5 wt% of nano-silica , D - 0.75 wt% of nano-silica, E - 1 wt% of nano-silica , F - 2 wt% of nano-silica

***Investigating the effect of diluting seawater on wettability change of oil-wet silica surfaces***

In this approach first we select Persian Gulf water as the basic fluid and then we dilute this fluid twice, 5 times, 10 times, 20 times and 100 times to create different low salinity. Then we put glass surfaces of oil-wet in these fluids for three days in ambient temperature but as it is clear on diagram these fluids do not have a significant effect on wettability change of silica surface. Therefore, we can say that low salinity in ambient temperature is not very active and cannot have any effect on silica surfaces wettability. This is shown in diagram 2 and Fig. 4. But we tested these fluids at 80 degrees and found that temperature is very influential on smart water performance and the more diluted smart water become, silica surfaces get closer to water-wet and in salt waters with 10 times, 20 times and 100 times, silica surfaces are completely water-wet which is shown in diagram 3 and Fig. 5. As you know, the used silica surfaces are free of clay and surfaces are just made of $SiO_2$ and according to the experiments in previous studies low salinity does not have a significant tension between water-oil interactions so there is another mechanism in these experiments. This mechanism refers to oil films stability. That is diluted salt waters with disjointing pressure destabilized its oil films and tear these films and replaces them. In this way silica surface wettability, tend to water-wet.

***Investigating the effect of different nanoparticles concentrations in the presence of low salinity***

Regarding previous experiments, we selected the salt water that is diluted 20 times as the basic salt water and scattered silica nanoparticles with different concentrations in it. As it is shown in the diagram, silica nanoparticles are unbelievably diluted in the presence of salt water. Even in low concentrations, they have

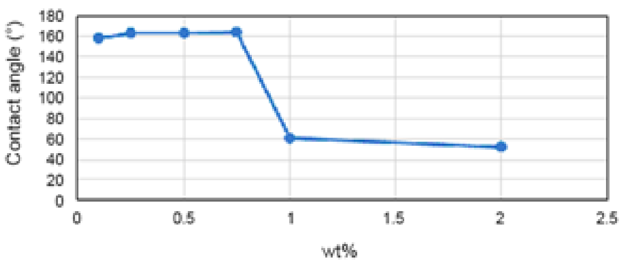


Diagram 1. Examining the effect of different concentrations of silica nanoparticles on silica surfaces wettability

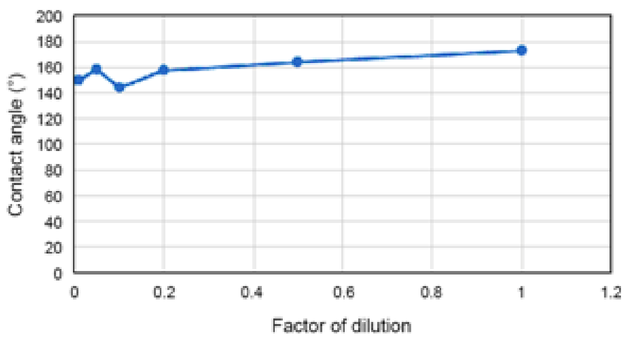


Diagram 2. Examining the effect of seawater diluting on wettability change of oil-wet silica surface

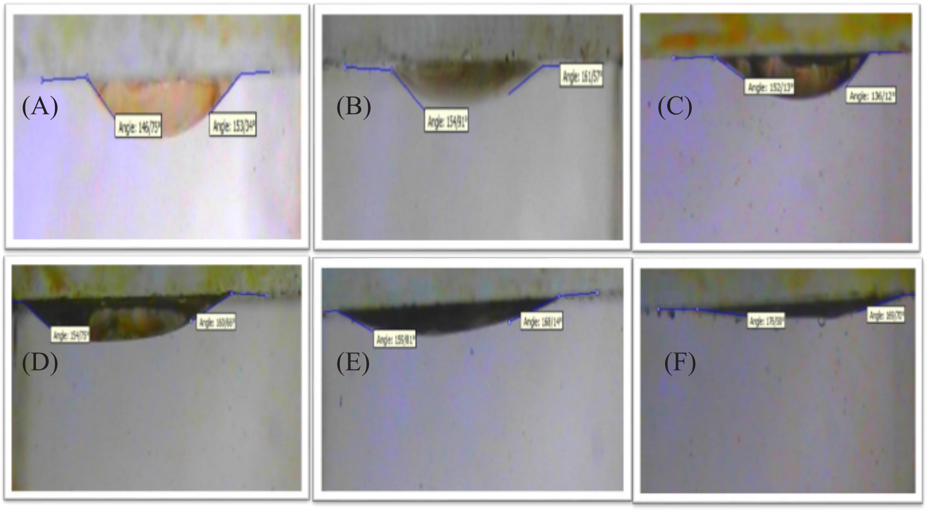

Fig. 4. A - 0.01% salinity , B - 0.05% salinity , C - 0.1% salinity , D - 0.02% salinity , E - 1% salinity , F - 0.5% salinity

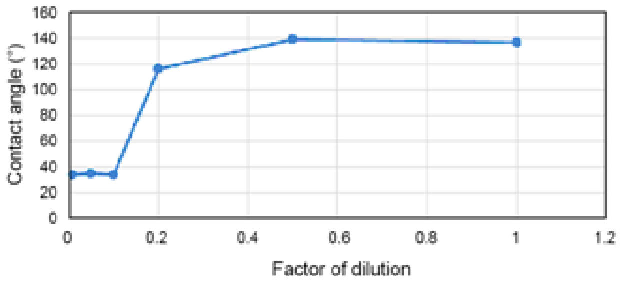


Diagram 3. Examining the effect of seawater diluting on wettability change of oil-wet silica surface in 80 degree centigrade temperature

changed silica surfaces wettability in ambient temperature while silica nanoparticles and low salinity were not able to change silica surfaces wettability in this way. Therefore, it can be concluded that the effect of low salinity and nanoparticles are very influential. In addition, these experiments indicate that silica nanoparticles sitting on surface is not the only reason for wettability change but structural disjointing pressure by nanoparticles and disjointing pressure by low salinity are in line with each other and fewer nanoparticles are needed for wettability change. Diagram 4 and Fig. 6 show the impact of different concentrations of nanoparticles in the presence of low salinity.

***Investigating effect of reducing amount of seawater salinity in combination with silica nanoparticles on wettability change of oil-wet silica surfaces***

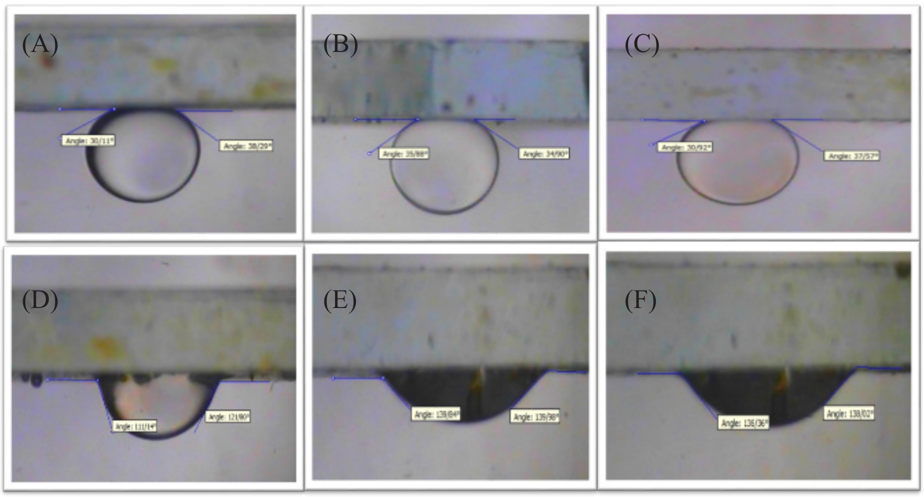

Fig. 5. A - 0.01% salinity at 80 degree temperature , B - 0.05% salinity at 80 degree temperature , C - 0.1% salinity at 80 degree temperature , D - 0.2% salinity at 80 degree temperature , E - 0.2% salinity at 80 degree temperature , F - 1% salinity at 80 degree temperature

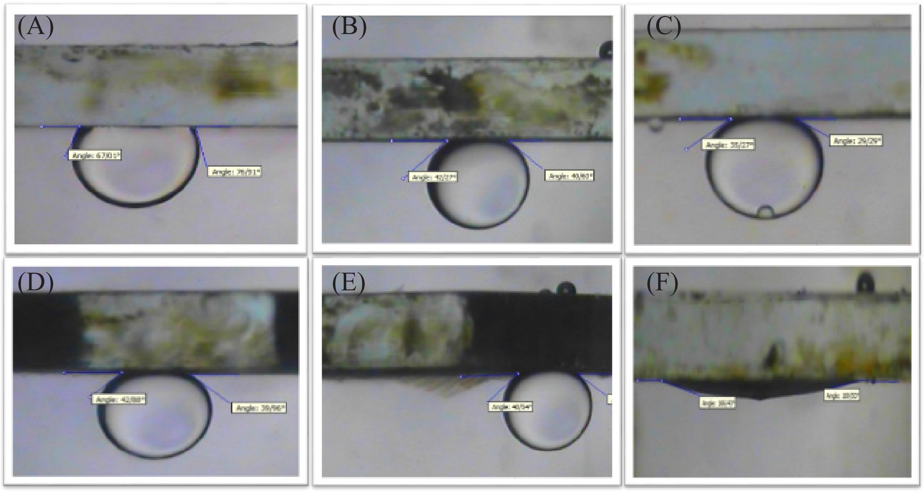


Fig. 6. A - low salinity and 0.1 wt% nano-silica , B - low salinity and 0.5 wt% nano-silica , C - low salinity and 0.75 wt% nano-silica, D - low salinity and 1 wt% nano-silica , E - low salinity and nano-silica in the endFigure , F - low salinity and 2 wt% nano-silica

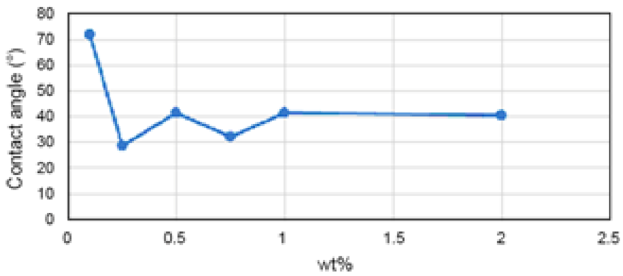


Diagram 4. Examining the effect of different concentrations of nanoparticles in the presence of diluted salt water

In this stage of experiment, once again we create diluted salt waters by using Persian Gulf seawater as the basic fluid. (Salt waters are diluted 0, 1, 2, 10, 20 and 100 times), then we add silica nanoparticles in concentration 0.25 wt to low salinity. As it is clear in diagram 5 and Fig. 7, when the salt water becomes more diluted, surface wettability tend to water-wet. However, by combining with seawater, silica surface wettability has not changed and in 100 times low salinity. The wettability does not change. This shows that the mechanism of disjointing pressure change is not possible by seawater and in 100 times low salinity it performs more like distilled water and silica nanoparticle by itself is not capable of removing oil from silica surface.

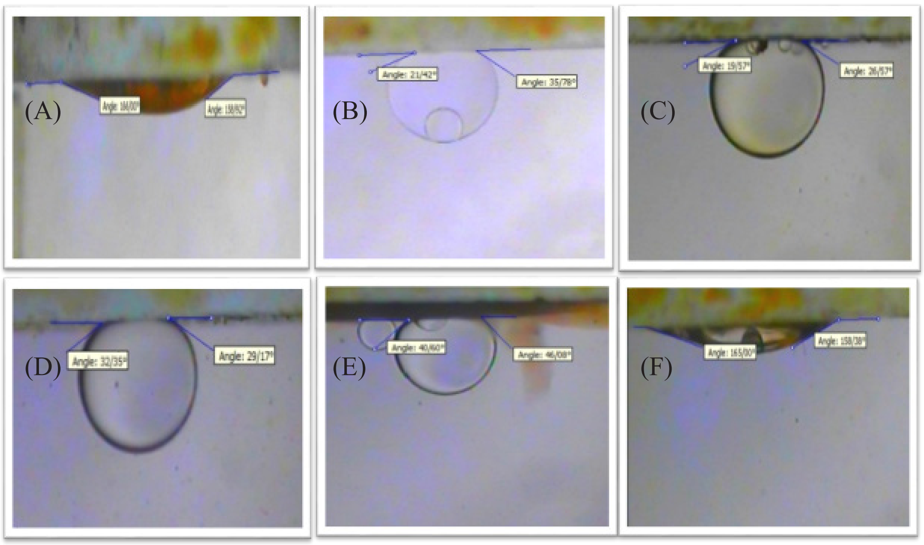


Fig. 7. A - 0.01% salt water and 0.25 wt% nano silica , B - 0.05% salt water and 0.25 wt% nano silica , C - 0.1% salt water and 0.25 wt% nano silica, D- 0.2% and 0.25 wt% of salt water and nano-silica , E 1% salt water and 0.25 wt% of nano-silica , F salt water, 0.5 and 0.25 wt% of nano-silica

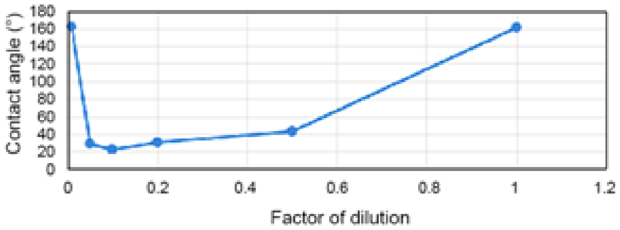


Diagram 5. Investigating effect of reducing amount of seawater salinity in combination with silica nanoparticles on wettability change of oil-wet silica surfaces

## CONCLUSIONS

The purpose of this research was examining the effect of different fluids including silica nanofluids, 20 times diluted salt water and the combination of these two fluids on oil production in oil-wet and water-wet porous media and with regard to this we can have the following finding:

- Using silica nanoparticles for oil production need high concentration which is affordable in terms of economy and silica nanofluids stability
- Using 20 times diluted salt water in ambient temperature has no impact on wettability change of silica surface but by increasing the temperature to 80 degree centigrade shows its effect and when the salt water is more diluted this effect is more significant.
- Oil-wet and water-wet of porous media is not the only factor controlling the distribution of fluids and different factors such as injected fluids material, their concentration and temperature are influential in oil production and fluids distribution.
- This research indicated that before wettability change different factors such as oil film instability, forming Pickering emulsions, improving rheology of injected fluids and reducing the surface tension are also influential in oil production efficiency.
- In general, using silica fluids combination and 20 times salt water have a significant effect on wettability and even much less concentrations of silica nanoparticles are needed. So this hybrid effect of enhanced oil recovery is highly recommended.

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