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RESEARCH PAPER

Liquid Repellency in Gas Condensate Reservoirs Using Different Chemical Treating Agents

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ABSTRACT

Liquid blockage decreases gas condensate productivity when the reservoir pressure near the wellbore falls below the dew point. Wettability alteration is the most promising method among various techniques to overcome the liquid blockage. In this study, the ability of different chemical solutions to change the wettability of rock types; carbonate and synthetic rocks from liquid-wet to a gas-wetting state was investigated. Contact angle measurement was conducted to evaluate the effect of the treating process. It was found that some of the best solutions containing COUPSYL®WRS nanofluid, PTFE, hydrophobic SiO_2 nanoparticles + PDMS, could change the water contact angle from 0° to 130.5°, 142.7°, and 155°, respectively. They could also produce water repellency conditions. In contrast, they were not effective on the synthetic rock surface. Moreover, the contact angle of condensate did not change by using these chemicals and remained at 0°. It was also shown that by increasing SiO_2 nanoparticle concentration from 0 to 2 wt%, the water contact angle increased from 117° to 155°, which was the most effective chemical solution in the wettability alteration process.

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1. INTRODUCTION

For decades, natural gas has been considered a cleaner and cheaper source of energy in comparison with other fossil fuels [1]. Natural gas reservoirs can be categorized as dry gas, wet gas, and gas condensate reservoirs [2]. Based on the composition of gas condensate reservoirs, they have been divided into two groups of lean and rich [2, 3]. The gas condensate reservoirs with relatively high heavy components are regarded as rich ones which drop out more condensate compared to lean gas condensate reservoirs. In the region away from the wellbore of a gas condensate reservoir, the pressure of the reservoir is above the dew point and the only present and flowing phase is the gas phase. During the production life, when the reservoir pressure drops below the dew point at reservoir temperature (between critical and cricondentherm), liquid drops out while the

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liquid phase is unmovable owing to the existence of capillary forces and low-liquid saturation. With lower pressure near the wellbore region, condensate saturation may increase to a higher value of critical saturation that could flow, and condensate blockage may accrue [4, 5]. These three regions are illustrated in Figure 1.

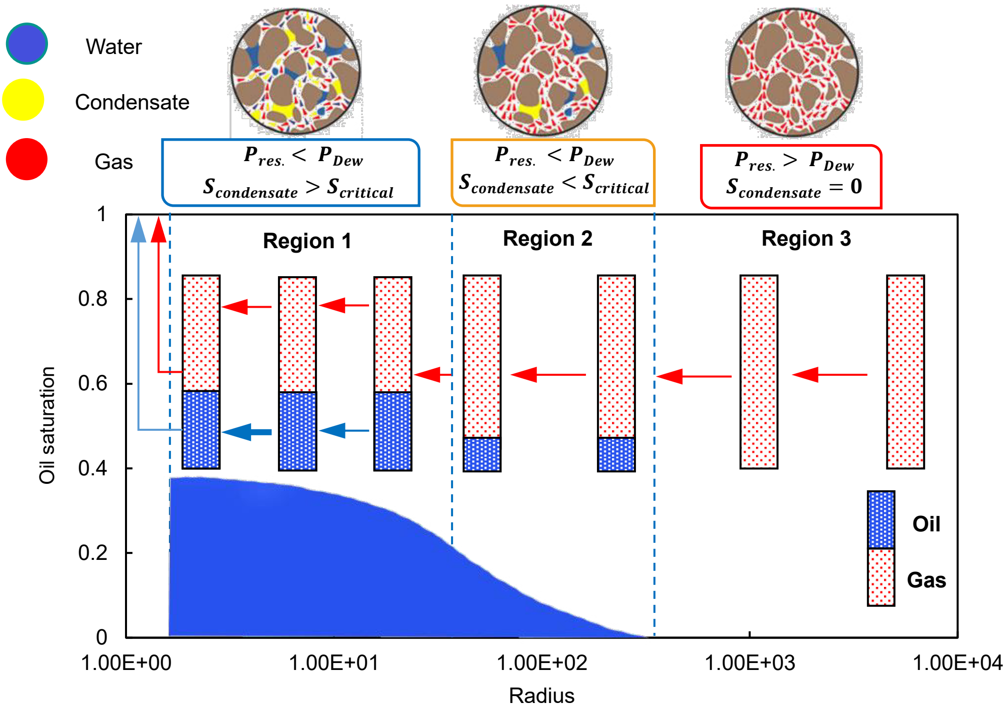


Figure 1. Three regions of flow behavior in a gas condensate reservoir

Gas production decreases by a factor of three to five because of liquids-condensate and water-blockage [3]. A lot of fields in the world confront this problem like the Arun field that the productivity of some wells decreased more than 50% [6]. It is important to note that, in the area far from the gas transport equipment, the condensate phase is more valuable compared to the gas phase. Therefore, finding an appropriate strategy to overcome liquid blockage around the wellbore and improve the gas and condensate production is essential. There are different solution techniques to increase the reservoir pressure and alleviate the condensate drop out including gas recycling, hydraulic fracturing, acidizing, drilling horizontal or slanted wells, water alternating gas injection, solvent injection, and chemical injection [7, 8]. Among them, chemical agent injection with its mechanism of wettability alteration is the most effective and the only permanent mitigation technique.

Gas condensate rock has an initially liquid-wetting state. The poor mobility (ratio of relative permeability to viscosity) of fluids in the strong liquid-wetting condition is the main factor of liquid blockage [9, 10]. The liquid-wetting condition results in spontaneous liquid imbibition due to the capillary forces and the liquid phase retained in the pore throat and body. Therefore, the liquid saturation increases and the gas permeability decreases [11]. During the wettability alteration process in gas condensate reservoirs, the rock surface affinity should be changed from liquid to gas, which means both water and condensate repellency is needed. This condition is called an amphiphobic state.

Different chemicals can produce hydrophobicity. Hydrophobicity is the ability of a material to repel water from its surface. This property is usually measured by placing a drop of water on a solid surface and then determining the angle that the drop forms with the surface. If the drop has an angle greater than 90 °, it will resemble a spherical drop and shows a hydrophobic behavior. If the drop has a contact angle of less than 90 °, it will be a very flat drop and will spread on the surface; it means that the substrate presents a hydrophilic behavior. Hydrophobicity has aroused worldwide interest during the past few years, which is due to its particular properties and potential applications including self-cleaning, automotive, oil and water separation, water purification, optical devices, medical and biomedical, anti-freezing, space and aerospace, and corrosion resistance. Furthermore, in gas condensate reservoirs, the presence of formation water leads to water blockage around the wellbore and in generally unsuitable conditions - well deliverability drops [12, 13]. Liquid water introduces the third phase to the gas condensate reservoirs besides the gas and gas condensate phases, by which the multiphase flow conditions may further decrease the effective permeability of the gas phase. Altogether, the hydrocarbon production may degrade further [14-18]. The water blockage also happens in the bulk of the reservoir, especially in tight gas reservoirs that have smaller grains and, thus, pore throats that lead to higher capillary pressure and higher irreducible water saturations, and so affect the permeability of the gas phase [19]. In the gas reservoirs, if the water sources are huge and the water permeability is high, the water invades the gas zone leading to a large amount of gas being trapped with significant decreases in its recovery factor [20, 21]. As a result, it is important to change the rock surface wettability into water repellency to improve productivity.

While hydrophobic surfaces decrease the water affinity to spread out, viscous liquids like oils or organic fluids and alcohols tend to stick and wet out these surfaces which are called oleophilic surfaces [22]. Most surfaces have oleophilic properties because oily fluids with low-surface tension tend to spread out on the surface. It is reported that there are enormous troubles in creating superoleophobic surfaces since most organic liquids have ultra-low surface tension. It is usually easy to make a superoleophobic surface against the high surface tension oily fluids, but difficult to prepare them to oils that have surface tension below 35 mN/m [23]. Hydrophobic surfaces show worse wettability and adhesiveness, and a smaller solid surface free energy compared to hydrophilic ones [24]. Figure 2 shows different contact angles of liquids and different forces which affect the wettability state.

The relationship between these forces, i.e. the surface free energy (surface tension) of the solid phase (γ_{SG}), the surface energy (surface tension) of the liquid phase (γ_{LG}), and the interfacial tension between solid and liquid (γ_{SL}) is expressed using Young's equation (Eq. 1) [25].

$$\cos\theta = \frac{\gamma_{SG} - \gamma_{SL}}{\gamma_{LG}} \tag{1}$$

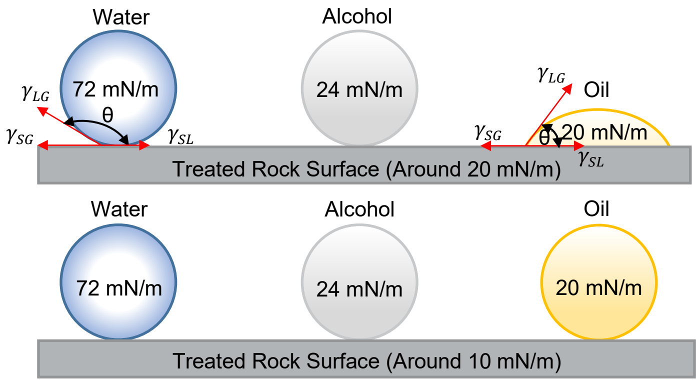


Figure 2. Schematic of the different components wetting condition in a three-phase system and the effective forces

where θ is the contact angle of the liquid on the solid surface. The contact angle is the angle formed between a liquid droplet and a solid surface at the point where the two meet. It is a measure of the degree of attraction or adhesion between the liquid and solid surfaces and so the wettability of the surface by the liquid. When a liquid droplet is placed on a solid surface, it can either spread out (wet) or bead up (not wet) [26]. The contact angle is determined by the balance between the intermolecular forces of the liquid with the solid (adhesion) and the intermolecular forces of the liquid with itself (cohesion) [27]. Therefore, a high- contact angle indicates that the liquid does not wet the surface well, while a low- contact angle indicates good wetting. The dominance of a force determines the wetting condition as summarized in Table 1.

Table 1. The relationship between forces affecting the wetting state

Energetic Relationship	Contact Angle (°)	Wettability
$\gamma_{SG} - \gamma_{SL} > \gamma_{LG}$	θ=0	Complete wetting
$\gamma_{SG} - \gamma_{SL} > 0$	0°≤θ≤90	High wettability
$\gamma_{SG} - \gamma_{SL} < 0$	90°≤θ≤180	Low wettability
$\gamma_{SL} - \gamma_{SG} > \gamma_{LG}$	θ=180	Non-wetting

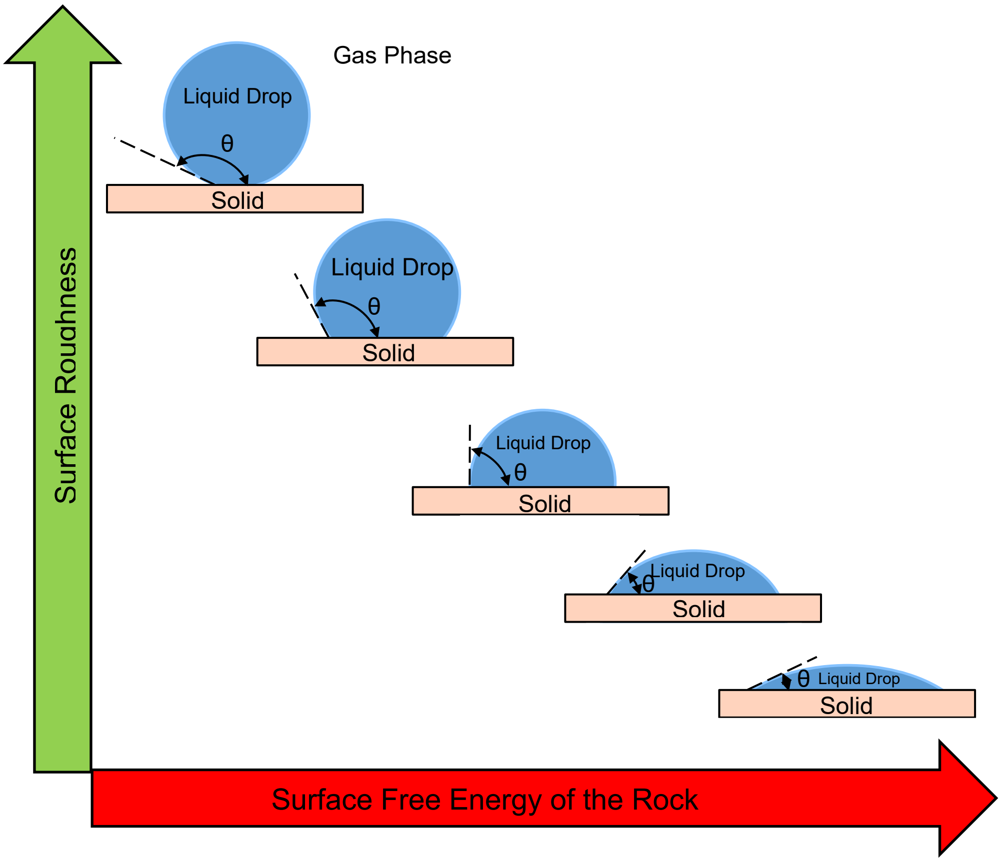


Figure 3. The impact of surface roughness and surface free energy of the rock on the wettability alteration

When the liquid contact angle is θ = 0° (corresponds to cos θ = 1), Young's equation produces $\gamma_{LG} = \gamma_{SG} - \gamma_{SL}$. If $\gamma_{LS} << \gamma_{S}$ and the surface tension of the liquid is less than the surface tension of the solid surface ($\gamma_{LG} < \gamma_{SG}$), the surface is wetted by the liquid phase; and if the surface tension of the liquid is greater than the surface tension of the solid surface ($\gamma_{LG} > \gamma_{SG}$), no wetting state is performed. As a result, to reach the low or non-wetting state, an important parameter decreases the solid surface free energy. It has been reported that water and oil repellency is provided by the fluoro and/or silane groups [28]. Fluorinated and perfluorinated chemical compounds have a key role in the wetting properties of the coating since they lead to surface energy reduction and in this way enhance the repulsive property of the coating against the deposition of any liquid [29, 30].

To enhance the recovery process, it is crucial to have a thorough understanding of the mechanisms that cause wettability alteration and how it affects the surface of the rock in the reservoir [31]. During the process of wettability alteration, the injected materials can either form a coating on the surface of the rock, which is referred to as coating, or they can remove the existing layer on the surface and cause the surface to exhibit different wettability, which is known as cleaning [32]. The chemical agents used in this process which are named wettability modifiers must exhibit specific characteristics including durability, affordability, unaltered performance, and resistance to thermal degradation.

The most effective approach for achieving a state of liquid repellency is considered to be the combination of a chemical composition comprising ultralow surface energy and a surface roughness that is suitably adapted (Figure 3). The application of nanoparticles can alter surface roughness, while fluorine functional groups can be utilized to decrease the surface free energy. The most efficient chemicals are fluorinated ones such as fluorinated nanoparticles. Due to its high electronegativity, fluorine is capable of strongly bonding with carbon atoms to form a short and robust C-F bond, which exhibits low reactivity, high thermal stability, and is not easily polarized, resulting in a substance with high-liquid repellence [33-35].

In a gas condensate reservoir, if the wettability changes from liquid-wet to gas-wet (increasing liquid contact angle), it can have several benefits, including improved gas recovery, reduced liquid dropout, enhanced well productivity, and reduced formation damage. The presence of a liquid phase can trap the gas and reduce the effective permeability of the reservoir. By changing the wettability to gas-wet, the gas can be made to preferentially wet the rock surface, allowing it to flow more freely and improve gas recovery. Also, the liquid phase can cause formation damage by blocking the pore throats and reducing the permeability of the reservoir. By changing the wettability to gas-wet, the liquid can be made to retract from the rock surface, reducing the potential for formation damage. Table 2 summarizes all the previous studies on using chemical agents on wettability alteration in gas condensate reservoirs. Different tests including contact angle measurement, capillary rise test spontaneous imbibition, entry capillary pressure, and coreflooding were performed to show that the used chemicals can change the wettability of different rock types to gas-wetting state.

2. Research Method

In this study, the ability of different chemical solutions to alter the wetting state of the natural carbonate rock and synthetic rock samples into a gas-wetting state was investigated.

2.1. Materials

2.1.1. Rock Samples

A limestone rock sample from a carbonate reservoir in the south of Iran was used. To study the wettability and to do the wettability alteration process, thin sections of prepared plugs were provided. The surfaces of the slices were polished to make them smooth and they were washed using distilled water. The slices were then dried in an oven at 60°C for 24 hours. Figure 4(a) showed the thin sections of carbonate cores. This rock type has a strong liquid-wet surface at its initial state i.e., before the treatment process. Another substrate was prepared using 3D printing. It is a novel and promising method to generate and replicate complicated designs such as porous rock production, which has various materials and pore geometries. Figure 4(b) shows the synthetic thin sections prepared by wire cut which are neutrally water-wet and strongly condensate-wet.

The mineralogical composition of the rock samples was determined using EDX and quantometry analysis for the carbonate and synthetic samples, respectively. They are shown in Table 3.

Table 2. Literature on altering wettability to gas-wet conditions using chemical treatment.

Chemical	Base Fluid	Porous Media	Tests for Wettability Alteration	Ref
FC754 cationic surfactant, FC722 Polymer with MW 100,000	Water based	Berea sandstone and chalk Porosity: 20.5-29 % Permeability: 1.47-1,089 mD	• Contact angle • Capillary rise test • Spontaneous imbibition • Entry capillary pressure • Coreflooding	[36]
Fluorochemical polymers FC-759 and FC-722 from 3M Company	Water based	Berea sandstone and chalk Porosity: 20-32% Permeability:1.3 -500 mD	• Coreflooding	[37]
Fluorochemical polymers FC-759 and FC-722 from 3M Company	Water based	Berea sandstone and chalk Porosity: 20% and 31% Permeability: 320 mD and 1.3 mD	• Spontaneous imbibition • Coreflooding	[38]
Different surfactants	Ethanol Water Water/ethanol Fluorinated solvent	Limestone	• Contact angle • Imbibition tests	[39]
Fluorochemical Surfactant 11-12P, Fluoroacrylate Copolymer L-19062 from 3M Company	Ethanol, water, acetic acid	Sandstone	• Contact angle • Spontaneous imbibition	[40]
30 wt% fluoropolymer in water	Water based	Sandstone Porosity: 10-20% Permeability: 0.2-5.0 mD	• Contact angles • Imbibition tests • Core flooding	[41]
Nonionic polymeric fluorinated surfactant, Novec FC4430 from 3M Company	Glycol-alcohol	Sandstone	• USBM wettability index	[42]
Fluorochemicals	Isopropyl alcohol, brine	Limestone	• Contact angle • Spontaneous imbibition	[43]
Synthesize Zirconium oxide (ZrO_2) nano-fluids	Water based	Carbonate	• Contact angle • Imbibition tests	[44]
Fluoroalkyl silane functionalized SiO_2 nanoparticles	Ethanol	Limestone Porosity: 28.4% Average pore diameter: 4.3 µm Permeability:1.5 – 2.0 mD	• Contact angle • Coreflooding	[45]
Polymeric surfactant	Ethanol	Limestone Porosity:25% Permeability:3-3.5 mD	• Contact angle • Imbibition tests	[46]
Anionic and non-anionic fluorosurfactants	Methanol	Carbonate, limestone, and dolomite	• Contact angle • Core flooding	[47]
Fluorochemical polymers Zonyl8740 from DuPont company	Water based	Sandstone	• Contact angle • Capillary rise test • Spontaneous imbibition	[48]
Anionic and nonionic fluorosurfactants	Water/ethanol	Carbonate Porosity: 20.8-29.5 % Permeability: 10- 122 mD	• Contact angle • Core flooding	[49]
Anionic fluoro-surfactant	Water/ethanol	Carbonate Average porosity:28.3 %	• Contact angle • Imbibition test	[50]

Chemical	Base Fluid	Porous Media	Tests for Wettability Alteration	Ref
Fluorohexyltriethoxy silane-SiO_2 nano composite	IPA and ethanol Water and methanol	Limestone Porosity: 27% Average pore diameter: 8µm Permeability: 2– 2.5 mD	• Contact angle Core flooding	[51]
Superhydrophobic TiO_2, SiO_2 and CNT	Fluorochemicals in alcoholic medium	Carbonate	• Contact angle and Spontaneous imbibition tests	[52]
Silicon-based molecules and fluoro-polymer in commercial SurfaPore M nanofluid.	Water based with very low volatile organic compound in commercial *SurfaPore M* nanofluid	Carbonate Porosity: 20% Permeability: 30 mD Sandstone Porosity: 24% Permeability: 190 mD	• Contact angle and • Spontaneous imbibition Core flooding	[53]
FG40, FP-2, and FG40 modified nano-silica	Water based	Sandstone	• Contact angle • Owens two liquid method • Glass capillary tube rise test • Imbibition tests	[54]
Fluorinated silica nanoparticle	Butanol	Sandstone	• Contact angle measurement • Coreflooding	[55]
Anionic commercial surfactant Silnyl®FSJ (SY)	Water	Sandstone	• Contact angles • Coreflooding • Spontaneous imbibition	[56]

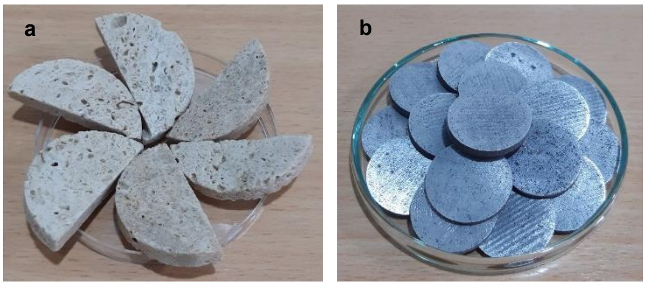


Figure 4. Slices of the a) Natural carbonate core sample, and b) Synthetic core sample

Table 3. Mineralogical composition of the used carbonate and synthetic rock samples

Carbonate Sample	**Elements**	**Ca**	**O**	**C**	**Mg**	**Na**	**Si**
	wt%	62.0	25.4	11.10	0.70	0.70	0.10
Synthetic Sample	**Elements**	Al	Si	Fe	Mg	Zn	Cu, Mn, Cr, Ni, Ti, Ca, Pb, Sn, V, Na, Bi, B, Ga, Cd, Co, Ag
	wt%	85.3	13.4	0.35	0.26	0.15	Each element <0.1 and Totally=0.54

2.1.2. Chemicals

In this study, hydrophobic SiO_2 nanoparticle in white powder form which was purchased from Merck Company was used. $CaCO_3$ nanoparticles were prepared using the cuttlebone of Sepia Pharaonis which were taken from the Persian Gulf beach and the powder was made using a mortar and pestle. Then the ball milling method as a physical method was used to reach the nano size (40-60 nm). Distilled water was used as the aqueous phase and the gas condensate sample obtained from a gas condensate reservoir in the south of Iran was used as the oil phase. Di-ethylene glycol which was prepared by the Jam petrochemical company was also used in contact angle measurements. Polydimethylsiloxane (PDMS) Sylgard 184 Kit with components of base (silicone elastomer) and the curing agent was prepared from Dow Corning, USA. Polytetrafluoroethylene (PTFE) 60 wt % in water was purchased from Merck Company. COUPSYL®WRS nanofluid, manufactured by Couple Shimi Sepahan Company, which is water-based, environment-friendly, and cost-effective was used to alter the wettability condition, and n-Hexane was used as the solvent. All the used materials are summarized in Table 4.

2.1.3. Chemical solution agents

Chemical A: 0.25 cc of PTFE 60 wt% was dispersed in 100 cc distilled water. The solution was homogenized using agitation on the stirrer at room temperature for about 1 hr and finally, the resultant solution was sonicated using an ultrasonic probe homogenizer for 20 min.

Chemical B: 1cc of COUPSYL®WRS hydrophobic nanofluid was added into 100 cc distilled water and agitation was done for about 1 hr using the stirrer and sonication was performed for more homogenization for 20 min.

Table 4. Used chemicals and their specifications, supplier, and purity

Chemical	Supplier	Purity
Hydrophobic SiO_2 nanoparticle	Merck company	99.8%
$CaCO_3$ nanoparticles	Own preparation using the cuttlebone	-
Distilled water	Laboratory water distillers	-
Gas condensate	Gas condensate reservoir in the south of Iran	-
Di-ethylene glycol	Jam petrochemical company	99%
Polydimethylsiloxane	Dow Corning, USA	96%
Polytetrafluoroethylene	Merck company	60 wt% in H_2O
COUPSYL®WRS nanofluid	Couple shimi sepahan company	Commercial production
n-Hexane	Merck company	95%

Chemical C: In preparing $CaCO_3$ nanofluids, distilled water was used as a solvent to suspend the nanoparticles. The base solution was prepared by adding CTAB (0.02 wt. %) to distilled water. Then the nanofluid was prepared by dispersing 0.1 gr of $CaCO_3$ nanoparticles in the base solution at room temperature. The solution was homogenized using agitation on the stirrer and the solution was sonicated using an ultrasonic probe homogenizer. Stability evaluation was also performed using zeta potential measurement.

Furthermore, the mixture of COUPSYL®WRS and PTFE and also a mixture of COUPSYL®WRS, PTFE, and $CaCO_3$ were also prepared and their effects on contact angle were investigated.

Chemical D: The solution was prepared by mixing hydrophobic SiO_2 and PDMS (10:1 PDMS base/curing agent (w/w) according to the manufacturer's instructions) in n-Hexane as solvent. The prepared solution was stirred at room temperature for about 1 h and ultrasonicated for 20 min. Table 5 summarizes the used chemical treatment agents in this study.

Table 5. Used chemicals and their concentrations in the wettability alteration process.

Treatment Agent	Concentration in the Base Fluid (wt%)
COUPSYL®WRS	1
PTFE	0.25
$CaCO_3$ nanoparticles	0.1
COUPSYL®WRS +PTFE	1+0.25
COUPSYL®WRS+PTFE+$CaCO_3$ nano particles	1+0.25+0.1
Pure COUPSYL®WRS	100
Hydrophobic SiO_2 nanoparticle+PDMS	0, 1, 1.5, 2+0.5

2.2. Treating Process

To conduct the contact angle measurement, carbonate and synthetic plates were cut into small plates and the dried slices were soaked in the prepared chemical solutions and heated at 60°C for two days. Then samples were removed from the chemical solutions and dried at 40°C for about 6 h, and finally, the contact angle measurements were done on the dried treated thin sections.

2.3. Contact Angle Measurement

A common quantitative technique for wettability determination is the contact angle measurement which is the liquid tendency to wet the solid surface and shows the wettability of the rock surface [57]. The drop shape on the surface relies on the surface tension of the fluid and the solid surface characteristic. The contact angle measurements can be performed either by the static method or the dynamic one [58]. The most widely-used method to measure contact angle on smooth and homogenous surfaces is the static contact angle or sessile drop technique in which a droplet of the liquid is settled on the solid surface, the phase boundary is fixed, and the angle between the solid-liquid interface using a camera is captured [59, 60]. The contact angle apparatus schematic is shown in Figure 5.

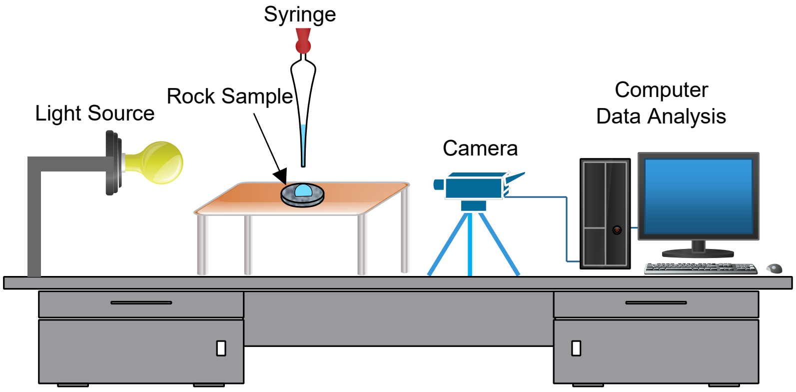


Figure 5. Schematic of sessile drop contact angle measurement apparatus

Table 6. Physical properties of the used Fluids at 25°C

	Density (g/cm^3)	Dynamic Viscosity (cp)	Surface Tension of Liquid/Air (mN/m)
Distilled water	0.997	0.890	71.97
Condensate	0.715	0.498	20.80
Di-ethylene glycol	1.118	35.7	44.80

The static contact angle of a sessile distilled water, condensate, and Di-ethylene glycol droplets on the rock surface before and after being immersed in different solutions was measured. The properties of the used fluids are reported in Table 6. The captured images of the droplets sitting on the solid surface in the presence of air were processed using Image-J software to extract the corresponding contact angles.

3. Results and Analysis

Figure 6(a) shows the results of the contact angle measurements of the water and oil droplets on the liquid-wet carbonate rock before the treatment process. If the oil phase has a very low surface tension, it could potentially lead to a situation where the carbonate rock appears to be both water-wet and oil-wet at the same time. This is because surface tension is a key factor affecting the contact angle between a liquid and a solid surface. Therefore, in a situation where the oil phase has a very low surface tension, it may spread out over the surface of the carbonate rock, effectively wetting it with a thin film of oil. At the same time, the water phase could also wet the surface of the rock, resulting in a low contact angle and a water-wet appearance. Figure 6(b) shows that before wettability alteration, the synthetic rock surface is neutrally water-wet with 92.6° of contact angle and strongly condensate-wet.

Table 7 illustrates the water and condensate contact angles. All the used chemicals could change the water contact angle significantly except the $CaCO_3$ nanofluid since the $CaCO_3$ nanoparticles are hydrophilic.

COUPSYL®WRS as a solution based on silane-siloxane can be used to create a hydrophobic surface on carbonate rocks. Silane-siloxane solutions are commonly used as water repellents on a wide range of building materials, including concrete, masonry, and natural stone. The silane-siloxane solution works by penetrating the pores of the carbonate rock surface and chemically bonding with the surface. The silane-siloxane molecules contain hydrophobic groups, such as methyl or ethyl groups, which repel water and prevent it from adhering to the surface of the rock. Hence, as can be seen in Table 5, the water contact angle increased from 0° to 130.5°.

PTFE is a synthetic fluoropolymer that is known for its non-stick and water-repelling properties. When the solution containing PTFE is applied to a carbonate rock surface, it can create a hydrophobic barrier that prevents water from sticking or

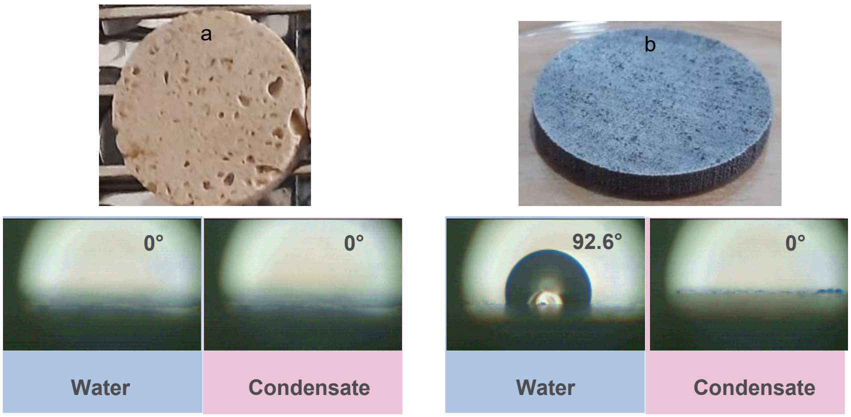
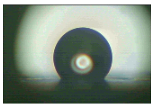
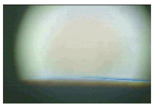
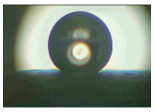
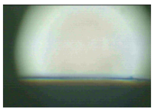
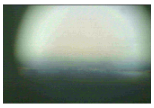
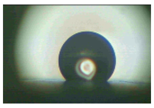
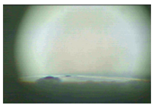
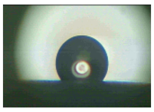
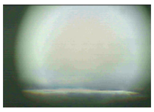


Figure 6. The static contact angle for the solid-liquid-air system before treatment on a) natural thin section and b) synthetic thin section

penetrating the surface. Carbonate rocks are typically composed of minerals such as calcite or dolomite, which are porous and can absorb water. When PTFE is applied to the surface of the rock, it forms a thin film that creates a barrier between the rock and the water. This barrier reduces the surface energy of the rock, making it difficult for water to wet the surface. The water-repelling properties of PTFE are due to its unique molecular structure, which consists of long chains of carbon and fluorine atoms. These chains are highly non-polar and have low- surface energy, which means that they are not attracted to polar molecules like water. As a result, water droplets will bead up and roll off the surface of the PTFE-coated rock, rather than sticking to it. The used solution containing PTFE can change the water contact angle from 0° to 142.7°.

Therefore, it is expected that the combination of these two substances would have a similar effect as each one, and the amount of contact angle would be between these two values, i.e. 135.9°. As expected, the fifth solution which is the combination of COUPSYL®WRS, PTFE, and CaCO3 nanoparticles, gives a contact angle value lower than both COUPSYL®WRS and PTFE and higher than CaCO3 nanoparticles. On the contrary, all the used chemicals can not change the condensate contact angle at all and its value remains 0°. PTFE and silane-siloxane are both hydrophobic coatings, meaning that they repel water. However, their effectiveness in repelling oils with low-surface tension may be limited. Oils with low-surface tension are typically non-polar, meaning that they do not have a charge separation between their atoms or molecules. This makes it difficult for hydrophobic coatings like PTFE and silane-siloxane to repel them because they are not attracted to the non-polar surface of the oil. In contrast, hydrophilic coatings are attracted to polar molecules such as water and are effective in repelling oils with low-surface tension. Such coatings have a higher surface energy and a more polar character, allowing them to interact with the polar head groups of the oil molecules and repel them. Therefore, if the goal is to repel oils with low-surface tension, it may be more effective to use a hydrophilic coating, rather than a hydrophobic coating like PTFE or silane-siloxane. Alternatively, a combination of hydrophilic and hydrophobic coatings may be used to achieve both water and oil repellency. It was found that the presence of fluorinated or every material which can produce low surface energy is essential to create the condensate repellency state.

Table 7. The contact angle of the carbonate sample (calcite) after wettability alteration using different chemicals

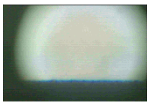
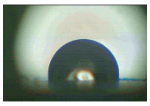
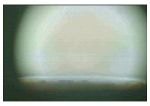
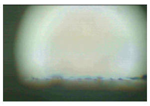
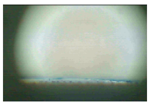
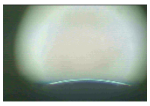
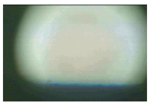
Chemical Solution	Concentration (wt%)	Water Contact Angle	Condensate Contact Angle
COUPSYL®WRS	1	 130.5°	 0°
PTFE	0.25	 142.7°	 0°
$CaCO_3$ nano particles	0.1	 0°	 0°
COUPSYL®WRS PTFE	1 0.25	 135.9°	 0°
COUPSYL®WRS PTFE $CaCO_3$ nano particles	1 0.25 0.1	 121.7°	 0°

As the surface tension of the used condensate was 20.8 mN/m, to achieve oil repellency, the solid surface tension should decrease below this value.

As shown in Table 8, the measured contact angles of both water and condensate were 0° on the synthetic rock surface except the water contact angle after the treatment with PTFE-containing chemical solution which was almost the same as before the treatment. Therefore, we can conclude that in the synthetic rock sample, all the used chemicals could produce neither water nor condensate repellency. Moreover, they were not suitable for the synthetic rock surface wettability alteration process.

The effect of SiO_2+PDMS solutions on the wettability alteration of natural carbonate rock is shown in Figure 7. Hydrophobic silica nanoparticles and PDMS are known for their water-repellent properties. By combining these two substances at the specified concentrations, the resulting solution can produce a high level of water repellency. PDMS is a silicon-based polymer that is made by polymerizing dimethylsiloxane monomers. It is known for its flexibility, biocompatibility, and low toxicity. PDMS has a low-surface tension which makes it useful in applications where wetting and spreading are important. The liquid-repellent properties of PDMS are due to its unique surface chemistry and texture. PDMS forms a low-energy surface that is highly hydrophobic, which means that it repels water. The contact angle of the three different fluids with different surface tensions was measured. It can be seen that by decreasing the surface tension from 71.94 mN/m to 20.80 mN/m the contact angle decreased to 0°, and the ability of the chemical fluids decreased to change the wettability of the surface. Furthermore, it can be concluded that at the same PDMS concentration which was 0.5 wt%, by increasing the concentration of hydrophobic SiO_2 nanoparticles, the water and Di-ethylene glycol contact angles increased, although the condensate contact angles were 0°. The molecular insight behind this is likely related to the ability of the hydrophobic silica nanoparticles and PDMS to interact with water molecules and prevent them from adhering to the surface of the material.

Table 8. The contact angle of the synthetic sample after wettability alteration using different chemicals

Chemical Solution	Concentration (wt%)	Water Contact Angle	Condensate Contact Angle
COUPSYL®WRS	1	 0°	 0°
PTFE	0.25	 91°	 0°
$CaCO_3$ nanoparticle	0.1	 0°	 0°
COUPSYL®WRS PTFE	1 0.25	 0°	 0°
COUPSYL®WRS PTFE $CaCO_3$ nanoparticle	1 0.25 0.1	 ~0°	 0°

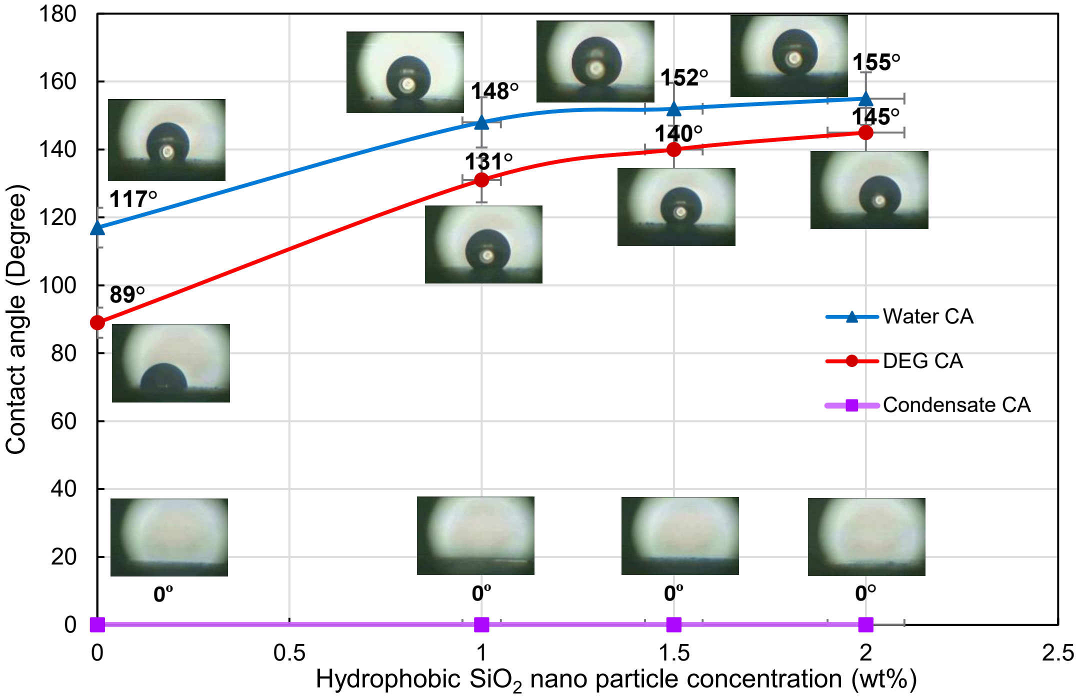


Figure 7. The static contact angle for the solid-liquid-air after treatment on natural thin sections

At the molecular level, the hydrophobic silica nanoparticles and PDMS likely create a surface that is highly unfavorable for water molecules to interact with due to their hydrophobic nature. The hydrophobic silica nanoparticles and PDMS molecules may arrange themselves in a way that create a surface with low-surface energy. This low surface energy makes it difficult for water molecules to adhere to the surface, resulting in high water repellency. Additionally, the hydrophobic silica nanoparticles and PDMS molecules may form chemical bonds or attractive interactions with each other, creating a stable and effective coating for achieving high water repellency.

4. Conclusion

In this study, the potential of different chemical solutions to change the wettability of natural carbonate rock and synthetic samples toward a gas-wetting state was investigated. Chemical solutions containing COUPSYL®WRS nanofluid and PTFE could indicate high water repellency on the carbonate rock sample. They could change the water contact angle from 0° to 130.5°, and 142.7°, respectively. Furthermore, the mixture of hydrophobic SiO_2 nanoparticles and PDMS was able to create a significant water repellency. It was found that by increasing the concentration of hydrophobic SiO_2, the water contact angle increased. Moreover, the various liquids including water, DEG, and condensate, with surface tension of 71.94 mN/m, 44.8, and 20.80 mN/m had a 0° water contact angle before the treatment. After wettability alteration, the water contact angle changed to 155°, 145°, and 0° respectively, which showed that higher surface tension of the liquid leads to higher liquid repellency. Among all the used chemical solutions, the combination of 2 wt% hydrophobic SiO_2 nanoparticles and 0.5 wt% PDMS, could produce the highest water repellency. Furthermore, when the $CaCO_3$ nanoparticles were used along with COUPSYL®WRS and PTFE, the water contact angle changed from 0° to 121.7 which was lower than using COUPSYL®WRS and PTFE alone, since the $CaCO_3$ nanoparticles are hydrophilic. However, none of the used chemicals could create the oil repellency property and so did not change the condensate contact angle on both the carbonate and synthetic core samples. The results of the contact angle measurement showed that although PTFE could produce high water repellency on the carbonate rock, it couldnot change the contact angle of water and condensate on the synthetic rock surface. COUPSYL®WRS nanofluid and also $CaCO_3$ nanofluid and a combination of them with PTFE lead to a more water-wetting state of the synthetic core sample. Therefore, the used chemicals are not suitable for changing the synthetic rock surface toward water repellency and probably the presence of another silane/ siloxane-based material and/or fluorinated chemicals is needed to reach the gas-wetting state.

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مقاله تحقیقاتی

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چکیده

زمانی که فشار مخزن در نزدیکی دهانه چاه به زیر فشار نقطه شبنم می‌رسد، تشکیل و به دنبال آن انسداد مایعانات باعث کاهش بهره‌وری چاه می‌شود. تغییر ترشوندگی از حالت مایع-دوستی به مایع-گریزی امیدبخش‌ترین روش در میان تکنیک‌های مختلف برای غلبه بر انسداد میعانی است. در این مطالعه، توانایی محلول‌های شیمیایی مختلف در تغییر ترشوندگی دو نوع سنگ کربناته و مصنوعی از حالت مایع-دوست به گاز-دوست مورد بررسی قرار گرفت. برای ارزیابی اثر فرآیند اصلاح خواص سطح، آزمایش اندازه‌گیری زاویه تماس انجام شد. نتایج به دست آمده نشان داد که برخی از بهترین محلول‌ها که حاوی نانوسیال COUPSYL®WRS، PTFE، و نانوذرات SiO_2 آبگریز + PDMS بودند، توانستند زاویه تماس آب را به ترتیب از ۰° به ۱۳۱/۵° ، ۱۴۲/۷° و ۱۵۵° تغییر دهند و شرایط آب‌گریزی را ایجاد کنند. در مقابل، هیچ یک از محلول‌های شیمیایی نتوانستند زاویه تماس میعانات را روی نمونه‌های سنگ کربناته و مغزه مصنوعی تغییر دهند. همچنین نشان داده شد که با افزایش غلظت نانوذرات SiO_2 از ۰ به ۲ درصد وزنی، زاویه تماس آب از ۱۱۷° به ۱۵۵° افزایش یافت که موثرترین محلول شیمیایی از میان محلول‌های مورد استفاده در فرآیند تغییر ترشوندگی این مطالعه می‌باشد..

نحوه استناد به این مقاله:

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