

Wettability Alteration Using Silane to Improve Water-Alternating-Gas Injectivity

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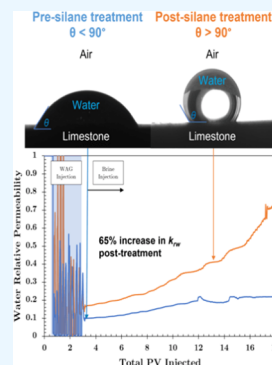
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ABSTRACT: Wettability is a main component that determines multiphase flow characteristics in a porous medium. Altering the wettability of a rock has a wide range of applications in the field of geosystems engineering, such as enhanced oil recovery, improving gas well deliverability, and geological CO₂ sequestration. Considering how injectivity in many field water-alternating-gas (WAG) processes is lower than expected, wettability alteration is especially suitable to address the reduction in relative permeability encountered during water injection. Several methods for injectivity improvement exist, including the use of surfactants, nanoparticles, salts, and alkalis. Using silanes to modify wettability has been a prominent technique in surface chemistry for decades but has very rarely been applied to porous mineral rocks, especially carbonates. This work explores the use of silanes to render sandstone and limestone surfaces more hydrophobic, thereby reducing gas blockage that causes injectivity loss. Contact angle measurements were taken and showed good wettability alteration away from water wet, exhibiting contact angles well above 90°, regardless of treatment conditions. Centrifuge tests were carried out, and the resulting residual fluid saturations and capillary pressure curves proved that the treatment is also effective on the pore scale. Corefloods conducted in sandstone and limestone cores showed a 45 and 65% increase in water relative permeability after WAG cycles after treatment, respectively. This translates directly to improvements in injectivity based on this treatment method.



INTRODUCTION

After relying on existing natural forces in a reservoir, primary production can only produce up to 10% of original hydrocarbons in place.¹ To produce the remaining oil, external energy must be provided to the reservoir through injection wells to maintain pressure and extend the life of producing wells. The two most common secondary recovery techniques involve waterflooding and immiscible gas injection. These methods can increase ultimate oil recovery by over 35%.² More oil can be recovered if the problems arising from secondary recovery are addressed. Particularly, waterflooding exhibits an unfavorable mobility ratio (greater than one), which reduces the sweep efficiency. This is even worse when using gas, as its viscosity is significantly lower than water viscosity.³ The combination of these injection methods, known as water-alternating-gas (WAG) processes, was proposed to take advantage of both the improved macroscopic displacement of waterflooding in the presence of an immiscible or miscible gas and the better microscopic displacement of oil by gas than by water.⁴ The validity of the WAG process was first established in 1958⁵ and has been demonstrated to be successful in numerous field applications.⁶

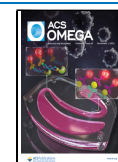
Despite WAG's success, recoveries have been lower than predicted. Abnormality in injectivity during WAG cycles is one of the main limiting factors preventing better performance.⁷ Injectivity is defined as the injection rate over the pressure difference between an injector and a producer.⁸ It can be applied

to both the water phase and the gas phase during cyclical WAG injection. Injectivity loss, therefore, can be defined as the reduction in the amount of water that can be injected for a given pressure differential. Similarly, it can be viewed as the increase in pressure needed to maintain the same water injection rate. There are several reasons that lead to injectivity loss, including reservoir heterogeneity⁹ and reduction of water mobility.¹⁰ The latter in specific can occur due to skin damage, poor injection water quality, or trapped gas near the injection wellbore. Concerns about injectivity loss have been raised since the early adoption of the WAG process,¹¹ and there exist several instances of injectivity loss documented in the literature, ranging from the microscale to the field scale. WAG experiments performed in high-pressure glass micromodels after waterflooding showed that the pressure-limited water injection rate decreased from 1800 barrels per day pre-WAG to about 800 barrels per day post-WAG after only two cycles. The micromodels showed that chasing water after gas slugs leads to gas snap-off and trapping, reducing the relative permeability of water.¹² A pilot project

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performed by Amoco in a West Texas oil-wet carbonate reservoir compared water injection rates before and after rich gas injection. Over an eight-month period, the initial water injection rate averaged about 350 barrels per day. Following two cycles of rich gas injection, the water injection rate dropped to a stable 100 barrels per day for the same injection pressure. Interestingly, the gas cycles show a decreasing trend in the injection rate, indicating that injectivity loss is not only encountered during the liquid cycle. The pilot scale results were consistent with relative permeability reductions observed in core-scale laboratory experiments.¹⁰ Another WAG field test in the Jay/LEC field in Florida and Alabama was carried out to determine if injecting nitrogen would result in a decrease in water injectivity. After the first cycle of nitrogen injection, water injectivity declined but at a decreasing rate. After the second gas cycle, it was decided to substantially increase the volume of water injected to see if it is possible to return to initial levels of injectivity. The decrease in water injectivity was 40% as compared to pre-WAG levels and only returned to that level after a large amount of water was injected. It is acknowledged that typical field WAG cycles are nowhere long enough to allow for such a remedy. The decline in injectivity was attributed to the reduction in water relative permeability due to higher gas saturation near the wellbore since laboratory experiments with core samples did not support attributing the reduction in water injectivity to asphaltene deposition or fine migrations.¹³ Many other WAG processes have reported injectivity loss issues for similar reasons.^{14–16}

Another mechanism that leads to injectivity loss is mechanical in origin and is mostly caused by the injected water. Formation damage in the form of permeability reduction or mud cake buildup can and does indeed reduce water injectivity. It has been shown that substantial permeability reduction might occur with an inappropriate water filtration system.¹⁷ The adverse effect of solid buildup at the sand interface, fine migration, and accumulation of biofilms in the well around the completion zone on water injectivity is also well documented.¹⁸ In such cases, the mitigation and remediation measures are relatively simple to implement, mostly involving proper water treatment and routine wellbore cleanouts.

It is established that water injectivity loss during WAG processes is a problem that needs to be addressed.⁷ The work presented here focuses on mitigating gas blockage—the phenomenon whereby the increased gas saturation around the wellbore during the gas injection cycle reduces water relative permeability, which in turn leads to a decrease in water injectivity. In two-phase flow, relative permeability is a function of the phase saturation, interfacial tension, and rock wettability. The treatment methods mentioned so far focus on the first two; however, the need for a longer-lasting solution for the problem of gas blocking led to the investigation of altering the wettability of the near wellbore. Wettability is defined as the tendency of a fluid to spread on the surface of a rock. It influences many of the two-phase flow characteristics, such as capillary pressure¹⁹ and relative permeability.²⁰ Extensive work has been done using fluorinated and polymeric chemicals to permanently alter the wettability of rocks in gas condensate systems. It was shown through contact angle measurements, spontaneous imbibition tests, and fluid flow tests in sandstone cores that the treatment is effective and permanent.²¹ Laboratory corefloods conducted using Berea sandstone cores showed a 65% increase in gas relative permeability and a 20% increase in oil relative permeability after treatment with a fluorochemical.²² This supports previous network model predictions that wettability

alteration near the wellbore is the most efficient way of increasing gas well deliverability.²³ A different approach is to use nanofluids to alter the wettability. Nanofluids are suspensions of nanoparticles in a carrier fluid such as water. Recent work done on sandstone and carbonate cores involving contact angle measurements, imbibition tests, and fluid flow tests showed significant alteration away from water wet to intermediate gas wet.²⁴ It must be noted that energy-dispersive X-ray data provided showed that the nanoparticles are organofluoride and silicon-based. Even more recent work demonstrated the ability of nanoparticles to alter the wettability of low-permeability sandstone rocks.²⁵ The same concept can be applied to WAG processes, where altering the wettability of the rock is employed to improve water relative permeability.

Recent investigations in the context of CO₂ trapping and storage focused on the effect of organic acid adsorption on cap rock wettability alteration. It is well known that wettability plays an important role in cap rock integrity in terms of structural and residual trapping of CO₂. Despite being present in low quantities in saline aquifers, organic acids can negatively impact storage capacity.²⁶ Specifically, it was shown that a small increase in organic acid concentration leads to an increase in both advancing and receding water contact angles at ambient as well as high-pressure high-temperature conditions, rendering the mineral surface CO₂ wet. The resulting hydrophobic nature of the samples is attributed to the chemisorption of carboxylic acid on the surface.²⁷ Fatty acids were also shown to make surfaces oleophilic depending on pH, brine composition, temperature, and acid structure, and calcite surfaces can be rendered oil wet.^{28,29}

In the field of surface chemistry, the use of organosilanes to modify surface wettability is ubiquitous. Using them in petroleum engineering has been proposed in the past as a way to generate oil-wet sandstone samples,³⁰ but only as recently as 2019 have they been studied for their water-blocking preventive potential. The focus of one research was to silylate sandstone cores using supercritical CO₂ (scCO₂) as a carrier fluid. Spontaneous imbibition tests in Berea sandstone samples showed a decrease in brine imbibition after treatment, and the relative permeability of water measured in ~200mD cores was 60% higher than that in the nontreated case. The gas relative permeability also exhibited an increase by 19%.³¹ A more comprehensive study was carried out with different silanes and different sandstone samples using either supercritical CO₂ or toluene as the silane solvent carriers. All combinations of surfaces, silanes, and carrier fluids resulted in a water contact angle of more than 140°, indicating that the surfaces were rendered hydrophobic, with a slight improvement when using scCO₂.³² Both of these studies investigated the use of silanes to alter wettability with a particular focus on the use of scCO₂ instead of conventional toluene to mitigate any environmental or safety concerns.

It is evident that wettability alteration is a promising method to improve water relative permeability in WAG processes. The most successful results for strong and permanent wettability alteration came from fluorinated chemicals, which is no longer a valid route to take. Their strong adsorption on mineral surfaces makes them persistent in soils and increases the risk of water contamination.³³ For the case of silanes, traditional toluene-based silylation is not applicable in the field, and modern scCO₂-based silylation restricts the type of gas that is used during WAG. There is a need for a more convenient method of altering the wettability of the near-wellbore region during WAG processes to

address injectivity losses in both sandstones and carbonates. The scope of this work includes qualitative and quantitative techniques to determine wettability alteration through contact angle measurements, centrifuge tests, and capillary pressure curves using sandstone and limestone samples. Finally, coreflood experiments are conducted in sandstones and limestones to evaluate the effectiveness of silanes in increasing water relative permeability and thus reducing water injectivity loss.

MATERIALS AND PROCEDURE

Rock Samples for Contact Angle Measurements. To determine the effectiveness of the treatment proposed in this work, mineral surfaces that are more analogous to reservoir rocks are used. This is in contrast to the idealized pure quartz or calcite surfaces used in traditional contact angle measurements and captures the added complexity of surface roughness and different mineralogy. A total of 24 Berea sandstone disks were obtained from a block with 20% porosity and a brine permeability of 60 mD, and 24 Indiana limestone disks were obtained from a block with 21% porosity and a brine permeability of 16 mD. These samples had a thickness of 5 mm and a diameter of 1 in. The sandstone samples were soaked in a 5 wt % hydrochloric acid (HCl) solution for 4 h to remove impurities, then rinsed with DI water, and oven-dried for 24 h. The limestone samples underwent the same cleaning step but using sodium hydroxide (NaOH) instead.

Rock Sample Treatment. The treatment of the samples for contact angle measurements was designed to study three variables: silane concentration, treatment time, and treatment temperature. The concentrations used were 0.5, 1, and 2 wt % silane in an alcohol–brine mixture that contains 95 wt % alcohol and 5 wt % brine. Treatment times were 1 and 24 h, and treatment temperatures were room temperature of 20 °C (RT) and 70 °C (HT).

Contact Angle Measurements. There exist several techniques to determine the contact angle formed by a liquid on the solid surface.³⁴ In this work, the contact angle formed by water on the solid sandstone and limestone samples was determined using the sessile drop method. A Ramé-Hart Model 250 goniometer/tensiometer was used with a microneedle that deposited the liquid drops on the samples, and the software DROPimage Advanced was used to measure the static contact angle. Each measurement was repeated five times to obtain a representative mean and standard deviation.

Rock Plugs for Centrifuge Test. The centrifuge used in this work is a Beckman model L5-50P Ultracentrifuge. It required that the plugs used have the dimensions of 1 in. in diameter and 1 in. in length. Four sandstone and four limestone plugs were cut from the same blocks used for the porous disks for contact angle measurements.

Centrifuge Test. The purpose of this experiment is to determine the residual fluid saturation in a treated sample and in an untreated sample. The rock plugs were first oven-dried for 24 h. Their masses were recorded to get the dry weight. Then the plugs were placed in a vacuum cell and vacuumed for 4 h. This ensures that the pore space inside the plugs was empty, which allowed for accurate porosity measurements as well as more uniform silane coverage. For the treated plugs, the vacuum cell was then filled with the silane and allowed to soak for 2 h. The untreated samples were filled with either water or dodecane. The mass of the fully saturated plugs was recorded, and the porosity was determined. The silane-filled plugs were then dried in the

oven until the same original mass was obtained to drain the pore space, and the same procedure of vacuuming and filling the cells with water or dodecane was performed. The mass of the filled plugs was measured again, and the porosity was determined a second time to validate the accuracy of the first measurement. The difference between the two measurements was within $\pm 1\%$, and the average porosity is reported in Tables 1 and 2. The plugs were centrifuged at 5000 rotations per minute (RPM) for 12 h. This was done three times to obtain an accurate mean and standard deviation.

Table 1. Sandstone Plug Porosities

sandstone	name	initial mass (g)	saturated mass (g)	porosity (%)
base case, water saturated	BWSS	28.92	30.65	13
treated, water saturated	TWSS	28.87	30.48	13
base case, oil saturated	BOSS	28.76	30.26	15
treated, oil saturated	TOSS	28.78	30.30	15

Table 2. Limestone Plug Porosities

limestone	name	initial mass (g)	saturated mass (g)	porosity (%)
base case, water saturated	BWLS	29.54	31.31	14
treated, water saturated	TWLS	29.27	31.01	14
base case, oil saturated	BOLS	29.35	30.71	14
treated, oil saturated	TOLS	29.63	30.80	12

Capillary Pressure Curve. The local capillary pressure can be related to interfacial tension (σ), contact angle (θ), and pore radius (r) by the Young–Laplace equation¹⁹

$$P_c = 2\sigma \cos \theta / r$$

For a given rock type, wettability alteration modifies capillary pressure by changing the fluid contact angle ($\cos \theta$). Therefore, capillary pressure could be used to evaluate the ability of silane to alter the wettability of the sandstone and limestone samples used in this work. The same centrifuge method used for the determination of residual fluid saturation was used to obtain the capillary pressure curve for each rock sample. This was done by measuring the mass of liquid centrifuged out of the core plugs after 30 min of centrifugation at a specific RPM. The RPM range was 200–5000. The capillary pressure was calculated using the following equation

$$P_c = 0.5\omega^2(\rho_w - \rho_{\text{air}})(r_o^2 - r_i^2)$$

where ω is the rotation speed in RPM; ρ_w and ρ_{air} are water and air densities (1.00 and $1.27 \times 10^{-3} \text{ g/cm}^3$), respectively; r_o and r_i are the characteristics of the centrifuge and bucket type used, where r_i is the distance from the axis of rotation to the top of the sample and r_o is the distance from the axis of rotation to the bottom of the sample.

Rock Cores for Coreflood Experiments. The same Berea sandstone (20% porosity, 60 mD) and Indiana limestone (21% porosity, 16 mD) blocks were used to make cores that are 1.5 in. in diameter and 12 in. in length.

Coreflood Experiments. The cores were first cleaned and oven-dried. Then, they were saturated with synthetic brine to determine porosity and permeability. After that, brine was

injected at a rate of 10 ft/day to simulate near-wellbore injection conditions during WAG processes. The steady-state pressure drop across the core was then recorded to get a baseline nontreatment measurement. Then, the WAG cycles started, with alternating 0.1 pore volume (PV) of nitrogen gas and brine to increase the gas saturation inside the core. After that, single-phase brine injection was carried out at the same rate to determine the extent of injectivity loss and how long it will take to regain initial levels of injectivity. The same procedure was then carried out on the treated cores. The coreflood setup is shown in Figure 1.

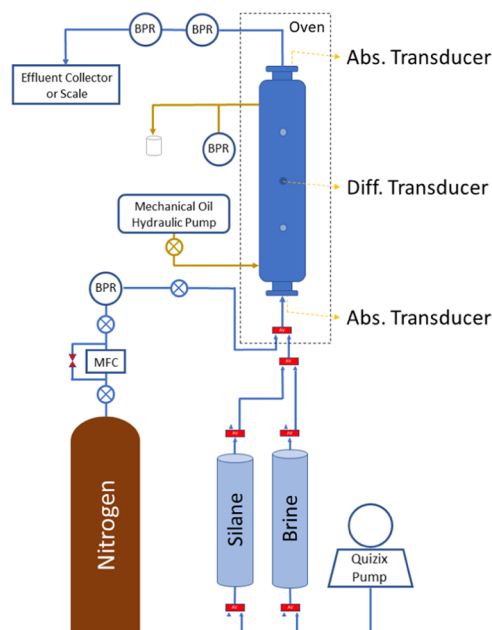


Figure 1. Coreflood setup.

Core Treatment Procedure. The treatment solution used consisted of 2 wt % silane in a 95–5 wt % solution of alcohol–brine. 4PVs of treatment solution were injected at 10 ft/day with no shut-in time for both fully brine-saturated sandstone and limestone cores. The cores were then flushed with brine to remove the treatment solution and prepare the post-treatment core for the same injection strategy as the pretreatment core.

RESULTS AND DISCUSSION

Contact Angle Measurements. The contact angle through water was measured for each combination of silane concentration, treatment time, and treatment temperature. The results are shown in Figure 2a for the limestone samples and in Figure 2b for the sandstone samples.

There was complete spreading of water on the nontreated limestone (contact angle was zero), indicating that initially, the sample was water wet. Pure calcium carbonate surfaces do not form stable bonds with silanes, so it is recommended to increase the hydroxyl concentration prior to treating the surface.³⁵ Therefore, the limestone samples were cleaned with NaOH. This leaves residual OH groups on the surface that, along with the water present in the treatment solution itself, improved silane coupling on the limestone surface.³⁶ Looking at the results in Figure 2a, the first observation is that all measured contact angles were above 90°, indicating a departure from water wet. Focusing on the silane concentration first, it is immediately apparent that an increase in silane concentration from 0.5 to 2.0 wt % did not result in any meaningful increase in the contact angle. In fact, the average contact angle for 0.5 wt % silane concentration is 115.5 and 116° for 1.0 wt % and 118.25° for 2.0 wt %. All measurements were within the standard deviation. Figure 2b shows the contact angle measurement results for the sandstone samples. These were treated with HCl to remove surface impurities that interfere with the stability of the covalent silicone–oxygen bonds.³⁵ The untreated samples showed complete spreading (contact angle of zero) of water, meaning that they were initially water wet. All measurements result in a contact angle above 90° except for the lowest concentration at the lowest temperature treated for the least amount of time.

Figure 3a shows the contact angle of the limestone sample vs concentration for different treatment times and temperatures. The 0 wt % silane is the pretreatment contact angle. The samples are initially water wet with a contact angle of zero (i.e., complete spreading of the water droplet on the surface). Comparing the treated samples, there is no significant change in the measured water contact angle at concentrations higher than 0.5 wt %. In fact, the average increase in contact angle from 0.5 to 1.0 wt % is only about 2%. Doubling the concentration to 2.0 wt % only led to an average of 1% increase in the measured water contact angle. Cleaning the limestone samples with NaOH before treatment may have contributed to the consistent contact angle measurement results with increasing silane concentration. Once

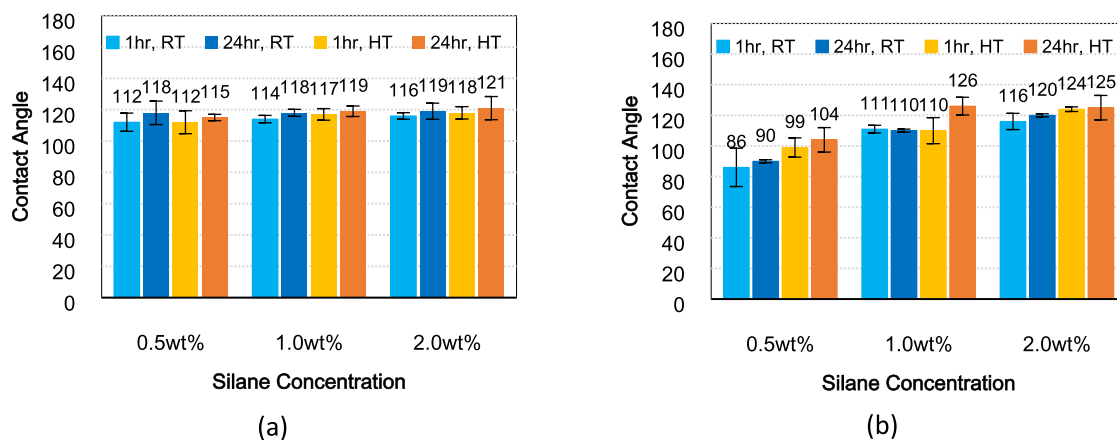


Figure 2. Water contact angles for (a) limestone and (b) sandstone.

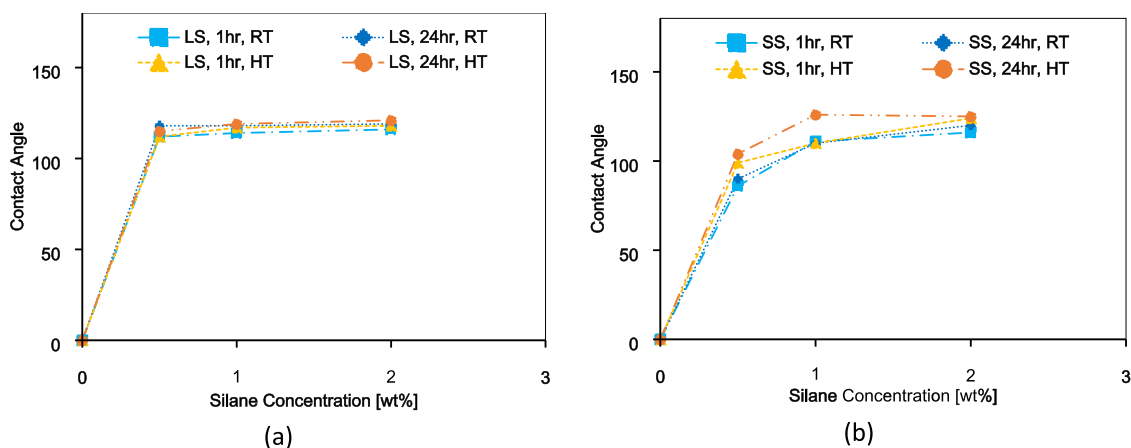


Figure 3. Contact angle vs silane concentration for (a) limestone and (b) sandstone.

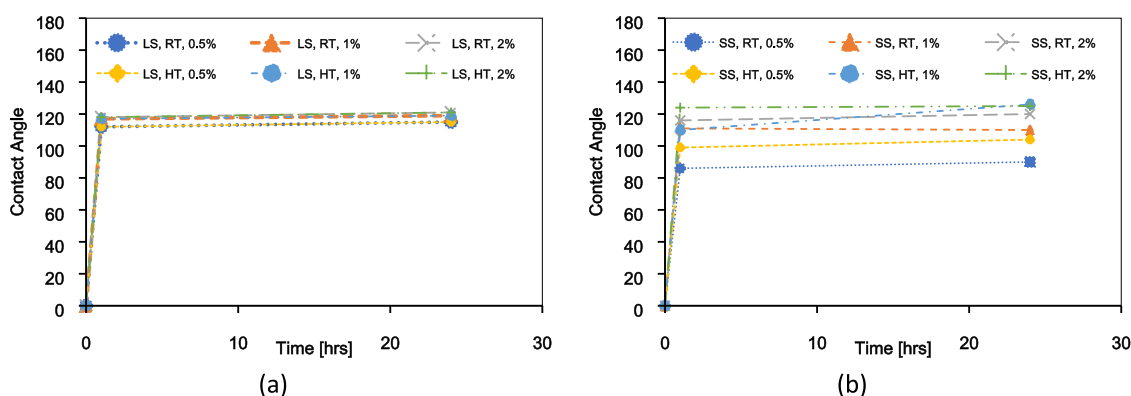


Figure 4. Contact angle vs treatment time for (a) limestone and (b) sandstone.

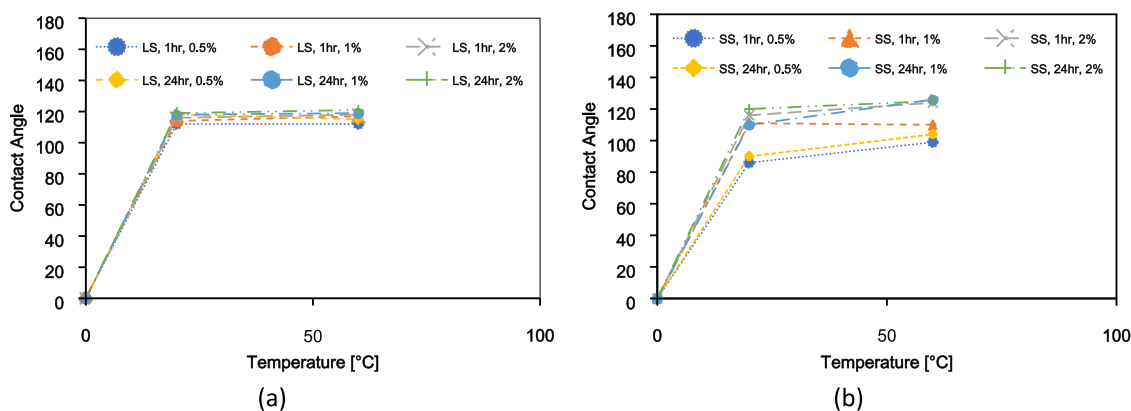


Figure 5. Contact angle vs temperature for (a) limestone and (b) sandstone.

all hydroxyl groups have coupled with the hydrolyzed silane, no more hydrophobicity can be induced. The results here show that a concentration of 0.5 wt % is sufficient to react with the most available hydroxyl sites, resulting in the maximum hydrophobicity, i.e., the lowest possible surface energy for this silane-surface pair.^{35,36}

Unlike the limestone case, it seems that the silane concentration does have a noticeable effect on the degree of hydrophobicity of the treated sandstone surface as seen in Figure 3b, especially for the 1 h samples. A higher concentration is needed to achieve a comparable level of hydrophobicity in the sandstone case. A 0.5 wt % silane solution treatment at room temperature for just one hour is not sufficient to produce a

properly hydrophobic surface. More time, higher temperature, or higher concentration is needed to bypass the minimum water-wet threshold of contact angle of 90°. The effect of temperature and treatment time is also in accordance with silane chemistry. The more time allowed for the reaction to occur, the more OH groups are reacting (hydrogen bonding), and the higher the temperature, the faster the coupling occurs (silane-surface bonding).^{36,37} Ultimately, this will not pose a problem in the final goal of treating the near-wellbore region to reduce injectivity loss as both injection time (analogous to treatment time) and reservoir temperature (analogous to treatment temperature) are typically much greater than that used in this work.

Regarding treatment time for both limestone and sandstone, it appears that one hour is sufficient to render the surfaces hydrophobic, regardless of treatment temperature or concentration, as seen in Figure 4a,b, respectively. It can be deduced that most, if not all, of the silanes already reacted with the surface at low treatment durations and temperatures.

It must be pointed out that it is difficult to relate the observed difference in the interaction between the treatment concentration and time to the difference in the cleaning methods used for the two mineral samples. However, these cleaning methods share the same objective, which is to maximize the surface coverage with hydrolyzed silane through its interaction with surface hydroxyl groups for maximum hydrophobicity. The surface coverage of silane may be different for different mineral surfaces even without involving these cleaning methods because of the difference in surface chemistry of the minerals by nature.

Finally, similar trends can be observed when the contact angle is plotted against temperature. RT (20 °C) is sufficient to generate hydrophobic surfaces for both the sandstone and limestone samples as shown in Figure 5a,b, respectively.

Therefore, a conclusion can be derived that the treatment with this particular silane is adequate enough to produce a hydrophobic limestone surface at a relatively low concentration, time, and temperature. In both the sandstone and limestone cases, silane treatment was successful in altering the wettability of the mineral surfaces away from water wet. It is worth mentioning that these contact angle measurements were made at ambient pressure and temperature. It has been reported that the hydrophobicity of organic-rich shale samples can be enhanced at higher pressures. It was also determined that the magnitude of this behavior is gas-type-dependent, as shown by advancing and receding water contact angles in CH₄/CO₂–shale–brine systems.³⁷ Similar results regarding the pressure dependency were shown for clay-coated quartz, and the clay coating was determined to increase hydrophilicity at higher temperatures.³⁸ The reason behind this wettability alteration can be attributed to solid–liquid interactions, which are dependent on the factors already mentioned. However, whether the effects of pressure, temperature, or salinity would also impact the hydrophobicity of the alkoxysilane-treated surface mentioned here is still an open question to be investigated.

Centrifuge Test. Treated and untreated limestone and sandstone samples were filled with dodecane or water and then centrifuged to determine their residual fluid saturations. The purpose of this test was to determine whether the silane can alter the wettability of the interior pore space, not just the exterior surface as proven by the contact angle measurements. Specific surface areas can be on the order of 30,000 cm²/cm³ (~1 m²/g),³⁹ so it is necessary to determine if the porous medium can be treated as easily as an exterior surface. Results are shown in Figure 6. Samples were treated with only one concentration of 2 wt % silane solution due to the long time needed to perform this experiment. For both rock types, the residual saturation of both oil and water was lower in the case of the treated samples (TW and TO) than in the case of the untreated samples (BW and BO). The original limestone samples showed an average residual water saturation of 45%, while the surface-modified samples only had 33% water remaining. This 27% decrease in water saturation indicates that there is indeed some degree of wettability alteration in the interior pore space away from water wet. Almost the same decrease was obtained in the oil saturation sample, indicating that not only is the sample less water wet but it also seems to retain less hydrocarbon as well. This is an

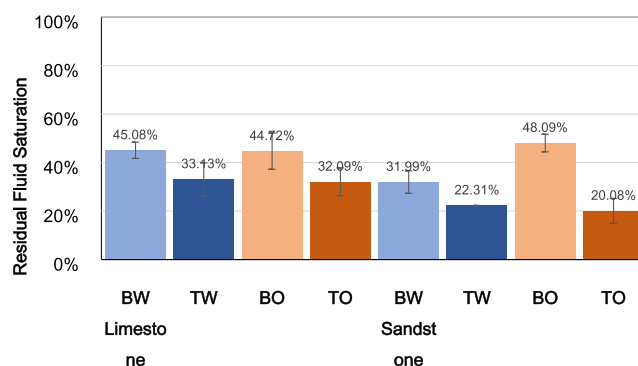


Figure 6. Residual fluid saturations after centrifuge test.

indication that there is a decrease in the total surface energy of the treated sample, which leads to less retention of any fluid.⁴⁰ The same trend can be seen in the water-saturated sandstone samples, where a 30% decrease in residual fluid saturation was observed. Interestingly, there is a 60% decrease in the residual oil saturation after treatment of the sandstone sample. This further shows that silane treatment is more effective in sandstones. Neither the limestone nor the sandstone sample used for this test was cleaned with NaOH or HCl, making this test more in line with real-world conditions. We can conclude that because of the lower residual saturations after treatment, it is easier for the liquids to be produced due to an increase in their relative permeability.

Capillary Pressure Curve. To further prove the efficacy of the silane in altering wettability and the effect this has on capillary pressure, a capillary pressure curve was constructed based on a centrifuge test with a treated (TWLS) and an untreated (BWLS) water-saturated limestone plug from the same block used throughout these experiments. The resulting P_c curves are shown in Figure 7.

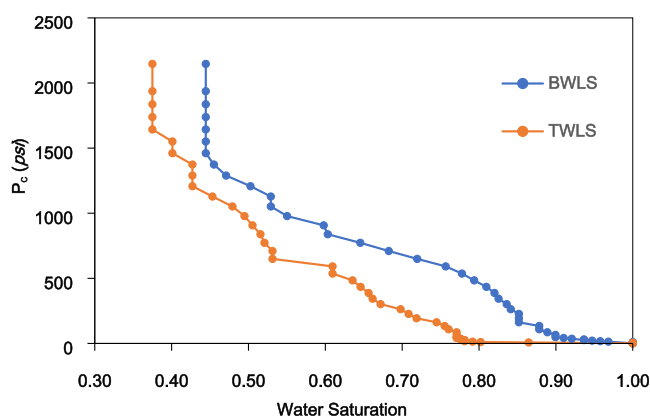


Figure 7. Capillary pressure curves for treated and untreated limestone samples.

The first thing to notice is that the two curves are roughly the same shape, with the treated curve shifted to the left. This follows from the Young–Laplace equation where if two samples have similar pore size distribution and are saturated with the same fluid, the reduction in the fluid contact angle will lead to a decrease in capillary pressure. Both samples here are limestones saturated with water; one is treated and one is not. It was established from the contact angle measurements that the silane treatment increases the contact angle θ , resulting in a decrease in

P_c . It is noted that the residual water saturation for the untreated plug is around 44%, while it is around 38% for the treated one. These results agree with the previous centrifuge test, reconfirming that the silane is indeed capable of reducing the surface energy of the interior pore space, which expels more fluids for the same pressure. For the untreated sample, the residual fluid saturation was reached at around 1460 psi. At that same pressure, the treated sample was still able to expel more water. It kept expelling water as the pressure increased until 1640 psi, at which it reached an irreducible water saturation of 38%. Less water remaining in the sample indicates that the treatment was successful in making the surface more hydrophobic. An important aspect of the capillary pressure curve is the initial point at which the resident fluid starts to come out. This is known as the displacement pressure P_d and can be an indication of the sample wettability. As it becomes less strongly wetted by one fluid, the pressure needed to displace it with another fluid decreases.¹⁹ The early time capillary pressure during water desaturation is shown in Figure 8.

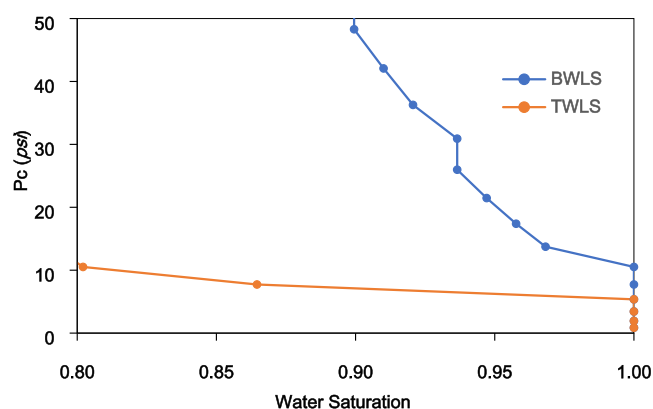


Figure 8. Displacement pressure.

As expected, the displacement pressure of the untreated sample is around 13.5 psi, higher than that of the treated sample, which is around 7.5 psi. This means that the initial pressure needed to start displacing the first drop of water out of the treated sample is lower, hinting at the reduction of rock affinity for water. As the gas displacement of water continued, the treated sample had less remaining water than the untreated sample at any given capillary pressure. All of the results discussed above are promising enough to justify the proof-of-concept coreflood experiments described in the following section.

Coreflood Experiments. Two proof-of-concept corefloods were performed to evaluate the ability of the silane to alter the wettability of the rocks substantially enough to induce an increase in water relative permeability after WAG injection. Table 3 shows the injection conditions for both corefloods. After initial porosity and permeability measurements, the cores underwent brine–nitrogen WAG injection, and the measured pressure drop was used to calculate water relative permeability.

Table 3. Coreflood Injection Conditions

total flow rate	10 ft/day
pressure	1000 psi
temperature	70 °C
treatment	4PV, 2 wt %

The results are shown in Figures 9 and 10 for untreated limestone and untreated sandstones, respectively.

For the limestones, the relative permeability of water is 1 before the WAG started. During the gas injection phase, the relative permeability sharply decreases. This is because it is difficult to achieve the same injection pressure when switching from liquid to gas in such a short injection cycle. When the initial gas pressure is high, the resulting relative permeability is low. This behavior is seen for both the treated and untreated cores. However, the effect of the gas is seen almost immediately without surface treatment of the limestone core, where the maximum water relative permeability was only about 0.55. This is because the water that is injected after a gas cycle is encountering resistance from trapped gas and competitive flow with mobile gas (i.e., relative permeability effect). Wettability plays an important role in capillary trapping. Since the core is water wet, gas saturation increases by the snap-off mechanism, which prevents newly injected water from flowing freely.⁴¹ After about 3PVs, WAG cycles stopped, and single-phase water was injected. The relative permeability to water at that point was calculated to be 0.1 for the untreated limestone core. It took about 30 PVs of water injection at 10 ft/day to regain initial levels of injectivity and a water relative permeability of 1, showing how long it takes to flush out all of the gas from the core.

For the treated limestone core, the first three WAG cycles show that the water relative permeability is not severely impacted by the presence of gas. This can be attributed to an increase in water permeability that results from the reduction of limestone surface energy associated with silane treatment. Gas mobility is also improved with a reduced tendency of capillary trapping in a less water-wet environment.⁴¹ This is consistent with the observed capillary pressure curve presented in Figure 7. After treatment, gas can displace water more easily, indicating that the surface is less water wet. However, the impact of the gas in the core can be seen after three cycles (around 1.6 PV): the water relative permeability decreased to a maximum of about 0.4. This is the injectivity loss in effect: for the same injection rate, a higher pressure drop is encountered because of the gas blockage effect, reducing the relative permeability to water. Comparing the pre- and post-treatment water relative permeabilities after the WAG cycles, there is a 65% increase in water relative permeability. As evidenced by the experiments presented thus far, the increase in water relative permeability can be attributed to the more hydrophobic limestone surface, which also reduces the effect of gas blocking. This in turn leads to better injectivity.¹² The treated core only needed 17 PVs of water injection to regain initial injectivity levels, a 57% decrease as compared to the nontreated core. While an alkaline pretreatment of the rock surface is intended to maximize the efficiency of silane treatment in the contact angle measurements, the coreflood results show a remarkable impact of silane treatment in the limestone core even without NaOH pretreatment. Future work is needed to determine whether a caustic preflush would actually enhance silane efficacy and thus be recommended for field application.

Regarding the sandstone core, the effect of gas blockage is immediately observed before treatment, with the maximum water relative permeability decreasing as more cycles are being injected. After 10 cycles, the water relative permeability is 0.25. After treatment, it was observed that the water relative permeability remained very high up until the last cycle. This shows that when water is being injected after gas, the effect of gas on the water relative permeability is significantly reduced with

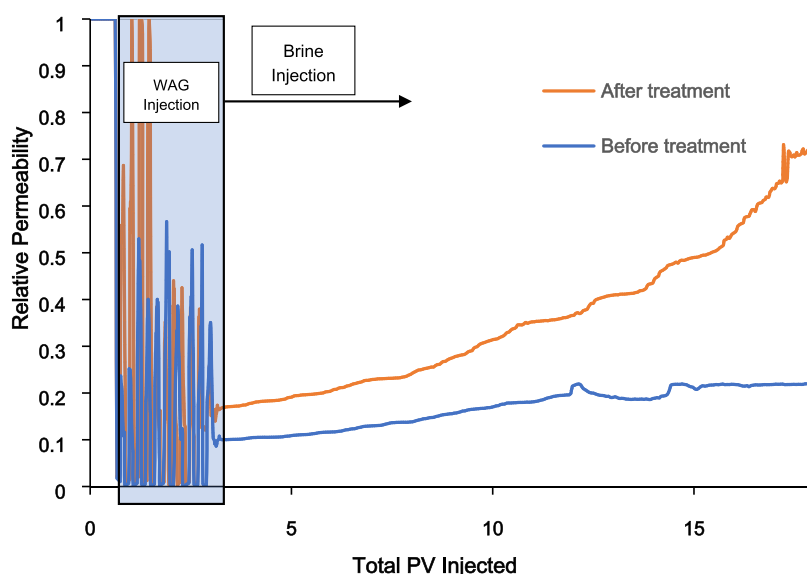


Figure 9. Relative permeability in limestone before and after treatment.

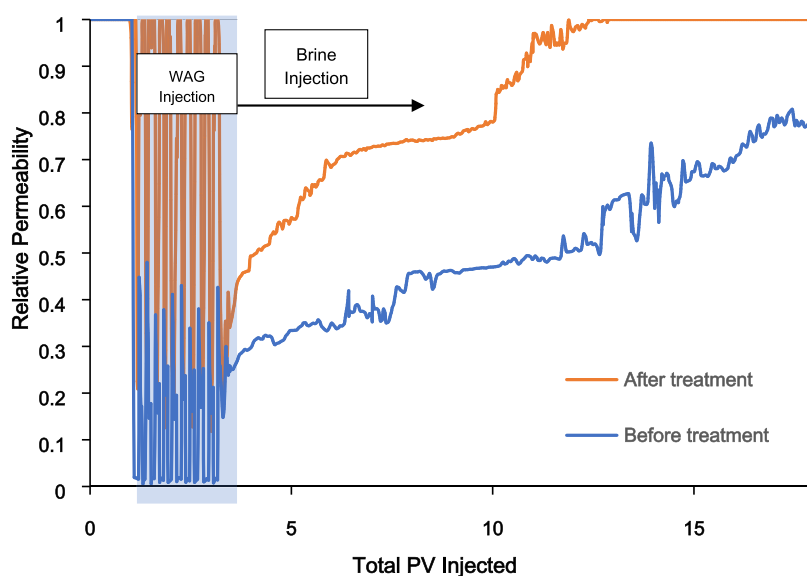


Figure 10. Relative permeability in sandstone before and after treatment.

the silane treatment that rendered the surface less water wet. At the end of the 10th cycle, the water relative permeability in the treated core was about 0.36. This is a 45% increase in water injectivity. The untreated sandstone took about 20PVs of water after the WAG to regain the initial injectivity levels, while the treated core only needed 10PVs. Such a change of the rate of increase in water relative permeability due to silane treatment may vary from well to well, depending on the severity of capillary gas trapping near the wellbore region, the injection conditions (pressure control versus rate control), and the degree and uniformity of reduction of mineral surface energy. The corefloods were done by injecting a fixed amount of water and gas every cycle for 10 cycles to establish a certain gas saturation inside the core, whereas a more realistic field application would be WAG injection at a fixed pressure. Translating the results presented here to a constant pressure injection field scenario, we can conclude that applying this silane treatment will allow more water to be injected between the gas cycles.

Looking closely at the water relative permeability during the WAG cycles (Figure 11 and Table 4), the impact of the silane treatment is also obvious. Figure 11a shows that water relative permeability is kept high in the first four cycles after treating the limestone core. This means that it took until the fifth WAG cycle to start trapping enough gas in the altered core to impede the flow of water (i.e., to induce gas blockage). Once this happens, a significant drop in relative permeability to about 0.4 is observed. For the sandstone case in Figure 11b, it took until the last WAG cycle to see reduction in water relative permeability. The difference between the limestone case and the sandstone case can be attributed to two factors: (1) the hydroxyl-rich sandstone surface is easier to silylate and (2) differences in rock morphology can cause significantly different fluid flow behavior (which is also why the permeability of the limestone is only 16 mD compared to the sandstone permeability of 60 mD). This latter reason can also help explain the centrifuge results shown earlier: the limestone sample saw an average of 27% reduction in

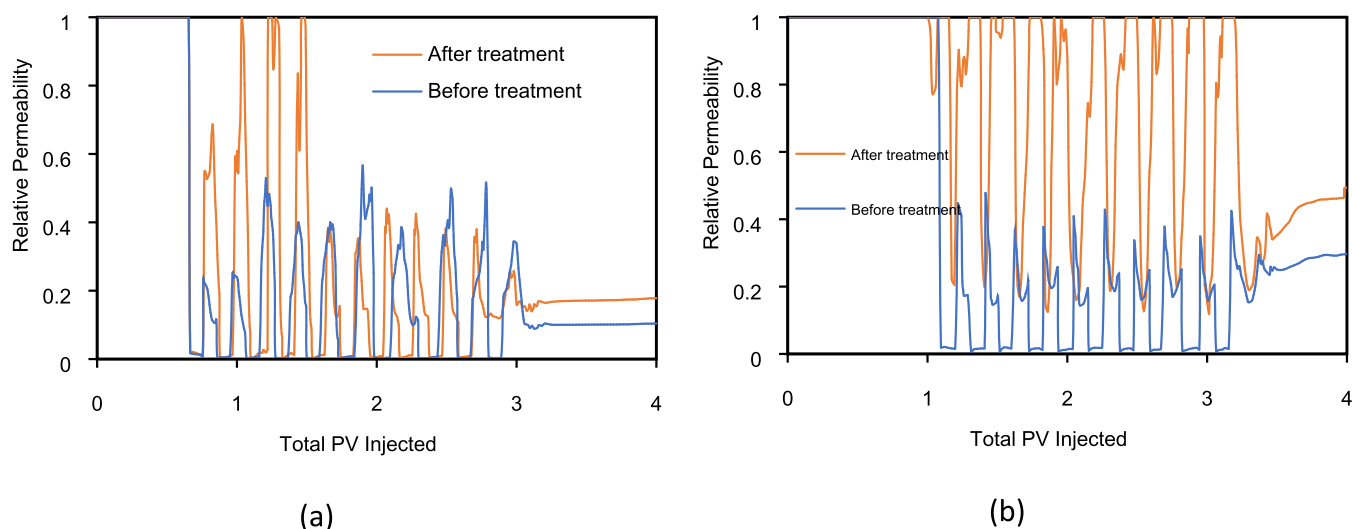


Figure 11. Water relative permeability during WAG for (a) limestone and (b) sandstone.

Table 4. Relative Permeabilities before and after Treatment

rock type	k_{rw} pretreatment	k_{rw} post-treatment	%change
limestone	0.101	0.166	+65%
sandstone	0.251	0.365	+45%

remaining fluid saturation, while the sandstone sample showed a 44% decrease in the remaining fluid saturation after treatment.

CONCLUSIONS

This work explored the use of silanes to reduce the surface energy of sandstone and limestone rocks to alter their wettability away from water wet. This will reduce injectivity loss encountered during WAG processes due to the increase in water relative permeability. The efficacy of the treatment was shown on the surface scale by contact angle measurements, which showed that even at low concentration, low treatment time, and low treatment temperature, it is possible to render both sandstone and limestone surfaces hydrophobic. Then, a centrifuge test proved that this treatment is also effective on the pore scale, where a lower residual fluid saturation was obtained for the treated samples compared to the nontreated samples. This was further shown to be the case with capillary pressure that was significantly reduced in the case of surface-treated limestone. Lower residual fluid saturation at all capillary pressures as well as lower initial displacement pressure was shown. Coreflood experiments in limestone and sandstone rocks showed that the silane treatment is effective in mitigating injectivity loss, evidenced by a 65 and 45% increase in post-WAG water relative permeability, respectively. Knowing that the carbonate-rich surface of limestones is difficult to silylate, the treatment effectiveness is attributed to the presence of water either in the treatment solution or on the rock surface. This increases the concentration of hydroxyl groups available to bond with the silane agent, imparting hydrophobicity to the limestone surface.

To the best of our knowledge, no work has been done on using silanes to alter the wettability of limestone mineral surfaces. The results presented here are the first to show that silane treatment can be a feasible approach provided there are enough hydroxyl groups present on the calcium carbonate surface, which is likely the case in the near-wellbore region of an

injection well in a WAG operation. These results indicate that silane treatment is a viable method of mitigating or even eliminating injectivity loss issues in sandstone and limestone reservoirs undergoing WAG processes. It is emphasized that the purpose of the treatment is to reduce the surface energy of the reservoir rocks as much as possible, which may result in a more oil-wet or, if possible, gas-wet surface. While oil wetness is unfavorable for waterflooding (but favorable for oil wetting due to improved pore-scale oil–gas contact) in the far field, this treatment targets only the near-wellbore region of WAG injectors and thus is not expected to impact the WAG EOR process in the far field. Whether a mixed wet condition (i.e., a mix of oil and water wet areas on the mineral surface) may affect the alkoxysilane treatment efficiency and effectiveness will be investigated in future work. Future work will also focus on understanding the surface chemistry involved between different silane structures and mineral surfaces and their impact on total surface energy.

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Notes

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