

Mini Review on Stability and Formation of Emulsion During Injection of Smart Water in Fractured Carbonate Reservoirs

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Abstract

One of the most commonly used methods of enhanced oil recovery for use in carbonate reservoirs is the smart water injection method. Asphalt nitic compounds in the oil serve as natural surfactants and form water emulsions in the oil when they are placed at the water and oil contact points. Besides, the salt contained in saltwater also contributes to the emulsion stability. Given that low-salty water and seawater are used for enhanced oil recovery, this process also increases the likelihood of the formation of W/O emulsions, so the assessment of the formation of W/O emulsions with low-salty water and seawater compounds and the stability of these emulsions due to the presence of different ions, can bring the conditions of formation of natural emulsions closer to actual events. Distinctive properties of injected water in order to form microemulsions of W/O and, the effect of concentration of ions in the injected smart water on the oil extraction efficiency have been investigated. Also, the formation of water emulsion in oil and its stability in oil sweeping in the formation in the case of smart water injection and its effect on the oil extraction efficiency have been discussed in full detail by presenting experimental results.

Keywords: Microemulsion, Smart Water, Self-Imbibition, Fractured Carbonate Reservoirs, Wettability.

Introduction

Considering the growing need for fuel and the limited oil reserves of the world, it is necessary to focus on increasing the extraction from oil reservoirs. Enhanced Oil Recovery is defined as a set of techniques and processes through which, the crude oil which cannot be extracted by conventional methods or is not economic and cost-effective, is extracted by using the energy or material out of oil field. Since the life of most of the world's oil reservoirs has reached the second half, the rate of oil extraction from them has been significantly reduced. For this reason, it is necessary to pay more attention to the enhanced recovery from oil reservoirs, [1].

The most important challenge in the oil extraction from fractured carbonate reservoirs, which results in a reduction in the percentage of oil recovery from them is the phenomenon of large amount of oil remaining inside the rock matrix network and clinging to the surface of the rock. There are two main reasons for this phenomenon, one is the state of carbonate rock wettability which is mostly observed in oil-wet reservoirs and the other is big difference is the low permeability in the rock matrix network and the high permeability in the rock fracture network. Due to the high permeability of the fracture network compared to the rock matrix network, when the oil is displaced by water, the oil in the fractures is rapidly discharged and a large volume of oil remains inside the rock matrix network. As a result, any process that can change the wettability state of the rock matrix network

to water-wet is an effective process in the enhanced oil recovery from fractured carbonate reservoirs, [2].

One of the most commonly used methods of enhanced oil recovery for use in carbonate reservoirs is the smart water injection method. In fact, by changing the salinity of the injected water and its ionic composition in this method, it is tried to minimize the interactional effects of water, rock and oil and, increase the efficiency of oil extraction from the reservoirs. Smart water was created by adjusting and optimizing the ion composition in the injected fluid to correct the initial wettability conditions of the rock.

Emulsions are used in most oil production sectors and enhanced oil recovery (EOR) processes, as well as in many cases, such as drilling, production, transportation and processing of crude oil [3-7]. Emulsion is defined as the dispersion of a fluid (liquid) in another liquid [8]. The emulsion stability is associated with the presence of particles located on the surface between the two fluids and postponing the tendency of the two fluids to detach [9]. These particles have usually molecules with polar and non-polar chemical groups in their structure, commonly known as surfactants. The dispersed phase is usually present in spherical droplets in the emulsion [10]. The separation of phases in the emulsion is influenced by the thermodynamics of the system. Because when the oil and water form two continuous phases, the distance between them and the free energy of the system decrease [11]. As

a result, the characteristics of the emulsion, such as the particle size, the average particle size, etc. cannot remain constant over time. Therefore, the emulsion stability refers to the ability of the dispersed phase to maintain its properties within a given time frame [12].

Characterization of emulsions is very common in most particle sizes. The emulsion structure is usually measured by the statistical distribution of the particle size. This measurement is important in several aspects [13-14]. Knowledge of the particle size distribution provides good information on the efficiency of the emulsification process [15]. In addition, observing any changes in the particle size distribution, such as the age of the emulsion provides useful information about the stability of the system [16]. Since the size of the emulsion droplets affects other properties of the emulsion, including its stability and rheology, valuable information can be obtained from these studies about particle size distribution. Most emulsions are naturally and thermodynamically unstable, which means they tend to separate into two separate phases over time due to the high surface interactions and the overall surface energy [17-18]. Therefore, the characteristics of emulsions including the distribution of particle size, average particle size and other characteristics change with time. The emulsion stability is determined by the behavior of the main parameters that are time dependent. There are several processes for breaking emulsions [19-20]. Physical instability mechanisms include sedimentation, creaming, aggregation, and coalescence [17-21]. In addition to these unstable physical mechanisms, mass transfer processes can also occur in emulsions [21].

Water can be found in three different forms in an oil system:

1. Solubilized water
2. Emulsified water
3. Free water

Depending on their capability and saturation, non-polar oils solve very little water. Beyond the oil saturation limit, water may be emulsified with oil in the presence of surfactants, or remain as a separate phase in the system [22]. Heavy polar components in crude oil, asphaltenes, waxes, and minerals such as clay and solid particles, temperature, droplet size, the distribution of droplets, pH of saline water and its compounds are among the factors

that affect the stability of emulsions [23-25]. Asphaltenes are one of the surfactants that are naturally present in oil [26]. They contain functional groups that consist of nitrogen or oxygen, and at the oil and water contact point, they may exhibit alkalinity, acidic, or acidic-alkalinity properties [27-28]. Asphaltene molecules typically contain hydrocarbons. These molecules also have a small amount of sulfur and oxygen [29-30]. The nitrogen content in these molecules is slightly less than sulfur and oxygen contents [31-33]. Although asphaltene molecules do not have a significant amount of polar components that can dissolve these molecules in water, polar compounds and components are present in sufficient amounts in these solutions to cause asphaltene molecules come to the water and oil contact surface [34-36]. The following section provides a review of studies on the role of surfactants and other organic and aqueous compounds in the formation and stability of emulsions.

Previous studies have also shown to some extent that surface activators alone can also be effective in changing the surface wettability, reducing the surface adhesion and enhanced recovery from the carbonate reservoirs, [37]. But large amounts of expensive chemicals are needed for field applications. Therefore, for economic reasons, oil companies are reluctant to implement this method in the field and the use of low-cost chemical additives is very important. Therefore, it seems that the combination of smart water and a small amount of surface activator as an injectable fluid can be used on a field scale.

Emulsion

Emulsion is actually an unstable thermodynamic system consisting of at least two phases of immiscible liquid, one phase of which floats in the other in the form of floating granules and reaches stability by a third substance called the emulsifier.

Figure 1 presents a view of the two phases of the emulsion, where A presents two immiscible phases, B indicates the non-dispersion of the first and second phases and the formation of a suspension, C indicates that the desired figure is unstable without the emulsifier and tends to return to its previous state. Finally, D means that the system stabilizes by adding the emulsifier and the droplets remain scattered.

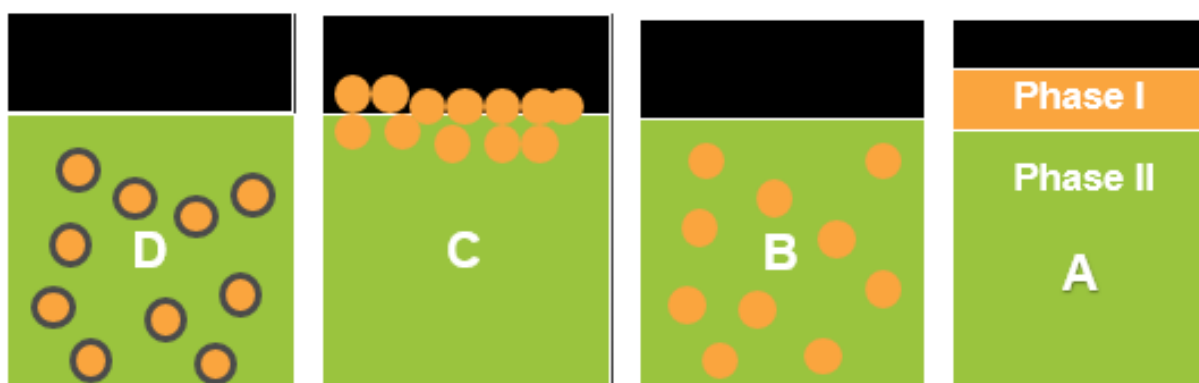


Figure 1: a view of the two phases of the emulsion

Emulsion preparation theory

As shown in Fig. 2, changing the state from A to B increases the contact surface between phase I and phase II and since the two phases are immiscible, the systems become unstable.

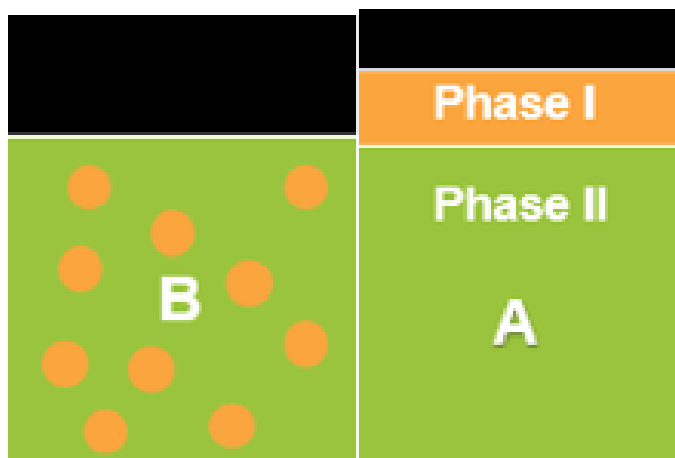


Figure 2: Changing the state from A to B

We actually add emulsifier to the system in order to reduce the surface adhesion between the two phases to form the emulsion. So in fact our goal is to reduce interfacial stress.

Classification of emulsions

We generally have three main categories for emulsions:

1. Simple emulsion: such as water/oil or oil/water;
2. Multiple emulsions: such as water/oil/water or oil/water/oil
3. Microemulsion

Emulsions are usually classified on the basis of stability, floating droplet size, flow rheology between phases, temperature, and so on. Also, the properties of emulsions and their stability may depend on the stirring speed used for preparing the emulsion as well as the formation time of the emulsion [38].

Microemulsions

Microemulsions are thermodynamically stable, that the droplets can be observed visually, usually consisting of two phases (water and oil), and surface activators are used to stabilize the system. Table 1 compares some properties of the emulsion and microemulsion.

Table 1: Comparison between some properties of the emulsion and Microemulsion

	Emulsion	Microemulsion
Clearness	Yes	No
Measure	10-12 mm	0.1-10 mm
Formation	Spontaneous	Need to an External force
Type	Oil/Water and Water/Oil	Water/Oil, Water, Oil/Water/Oil
Stability	Thermodynamically stable	Thermodynamically nonstable
Viscosity	Low viscosity, 20%-40%	Viscos

Emulsion inversion

An emulsion is called invertible if the scattered phase can be replaced by a solvent phase, this is usually possible by methods such as adding electrolyte, adding $CaCl_2$, or changing the volume ratio of the phases.

Emulsifiers

The third substance that makes the emulsion stable is called the emulsifier, and its task is to reduce IFT; in fact, surface activators are substances that reduce the interfacial stress between phases. Surface activators have different models classified as anionic, cationic, etc. Examples include clay particles, chemical additives, crude oil compounds such as asphaltene, waxes, resins and petroleum acids. Choosing the right surface activator depends on several factors, including pH, emulsion salinity, and system temperature.

Emulsion preparation

Basic points for preparing an emulsion include:

1. The liquid phase contains scattered droplets
2. Suitable volume ratio of phases for mixing
3. Selecting a suitable emulsifier for system stability

There are two points to keep in mind for preparing an emulsion:

1. The dripping phase must be created by a force scattered in the other phase.

2. Then fix these drops.

External energy can be found in many forms:

1. Heating
2. Homogenization
3. Creating turbulence

In the enhanced oil extraction process, we usually use gearbox oil as the scattered phase and saline water as the solvent phase to prepare the emulsion used in the oil well. Undoubtedly, emulsifier or surface activator is used to stabilize the emulsion. The solvent is stirred at different speeds over time depending on the needs and different characteristics of the solution to reach the desired system.

The overall design of the emulsion for each well is based on trial and error, and the best emulsion used for the well is prepared in this way. However, it contains a special oil injected into the reservoir. In preparing the emulsion, we must keep in mind that our chosen surface activator plays a very important role because its task is to reduce the interfacial stress of the reservoir oil to be produced through it. Also the emulsion formulation we are preparing, In addition to depending on the characteristics of the emulsion itself, it may change according to the condition of the reservoir and the condition of the reservoir.

In addition to all these factors, controlling the mobility of the

emulsion during operation is also very important. Emulsion mass design should be based on reservoir temperature, salinity of water remaining in the reservoir and type of crude oil in the reservoir because not observing these cases may make it difficult for us to control the fluid [39].

The role of emulsions in enhanced oil recovery

After preparing the emulsion and examining and controlling the related factors, we will investigate the events inside the well and the reservoir after the emulsion injection. In fact, injecting emulsion into the well does not break the oil resistance to dissolving in water, but lubricates the oil and improves production.

ASP microemulsions (alkaline, surface activator and polymer) and emulsifying agent are emulsions that allow the remaining oil trapped in the reservoir to be transported and produced. Other factors in the success of using this method are correct mass design and selection of a suitable design for mass injection, as well as attention to the rock and fluid dispersions of the reservoir.

One of the most effective emulsions for injection is the type of emulsions with the scattered droplets with slightly larger size compared to porous space cavities in the reservoir. Factors affecting the mobility of emulsion masses in wells depend on the composition of the masses, the amount of water used, the electrolyte content in the mass, the type of hydrocarbons and the amount of emulsifiers.

Figure 3 shows an image of a depth section of the reservoir that was initially fully integrated. We inject some water and surface activator through the injection well so that the oil in the reservoir makes an emulsion and reduce the interfacial tension between the water and the oil, increasing the mobility of the oil remaining in the well and producing it.

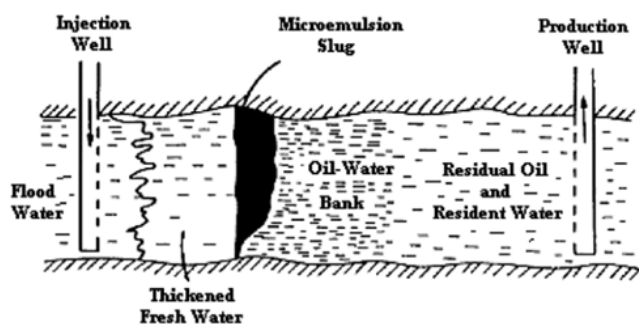


Figure 3: Image of a depth section of the reservoir

Smart water

In total, oil extraction includes three primary, secondary and tertiary methods, in the primary method 5-10% of oil, in the secondary 10-40% and in the third method more than 40% of oil can be extracted.

EOR methods include:

1. Thermal such as hot water vapor injection or combustion
2. Injection of gas such as N₂, CO₂ and fluency
3. Chemical methods such as surface activators, polymers and alkalis
4. Biotechnological methods such as MEoR/MIoR

We more focus on chemical methods.

The most important mechanisms in smart water injection are:

1. Change in wettability
2. Reduced interfacial tension
3. Reduced asphaltene deposition

Mechanism of reducing interfacial tension

In smart water, the injection of ions such as NaCl, CaCl₂, MgCl₂, CaSO₄ and MgSO₄ are injected, which are ionized to positive and negative ions in water, that is, to cations and anions that, cations forms the complex with negatively charged asphaltene and they are located between the surface of water and oil. Asphaltene acts like a surface activator with the polar part on the water side and the non-polar side on the oil side, which causes the formation of water-in-oil or oil-in-water emulsions. Oil-in-water emulsions stabilize the injection front and are useful. But water in oil emulsion has some advantages and disadvantages [40].

Disadvantages of water emulsion in oil are:

1. Increased oil viscosity
2. Increased hydrostatic pressure in the well column
3. After enhanced oil extraction, we need a series of separators to separate from each other.

The advantages of water emulsion in oil are:

1. Increasing the relative water permeability in the EOR method
2. Increased mobility ratio or MR
3. Increased oil reciprocation efficiency

1 < MR causes the phenomenon of fingering, i.e. instead of pushing, the oil itself moves faster and reaches the production well.

At MR > 1 there may be no ability to push oil.

The best case is MR = 1.

Types of emulsions include:

1. Water in oil emulsion where the surface activators are around water, the polar part of which is on the water side and the non-polar part is on the oil side.
2. Oil in water emulsion
3. Multiple emulsions

The mechanism of change in wettability is that the cations form a complex with the asphaltene that is on the surface of the rock and are located between the surface of water and oil. On the other hand, anions such as SO₄²⁻ are absorbed by the rock surface and when their expansion exceeds a certain limit, they reject the oil and more oil is produced.

Smart water tests and low salinity on carbonate rocks Self-imbibition experiments

Webb et al. (2005) examined the effect of sulfate ions on oil extraction efficiency from North Sea carbonate rock by a spontaneous imbibition experiment on the core. They found that the injection of seawater into the carbonate rock changes the wettability of the rock and made it more water-wet than injecting sulfate-free water, [41]. In 2007, Zhang et al. studied the change in wettability of the North Sea chalk reservoirs in the Eco physical Field. They investigated the effect of adding calcium and magnesium ions to water for injections on the oil extraction efficiency. According to their results, if the injected water contains sulfate and calcium ions or sulfate and magnesium ions, the wettability of the rock will change, [42].

In 2008, Strand et al. performed self-imbibition and force-induced imbibition tests on the carbonate rock confirmed the improvement of the water-wet nature of the carbonate rock after the injection of seawater at high temperature which led to an increase in oil production, [43]. Figure. 4 shows the effect of seawater injection on the efficiency of oil extraction relative to the formation water in both self-imbibition and force-induced imbibition states.

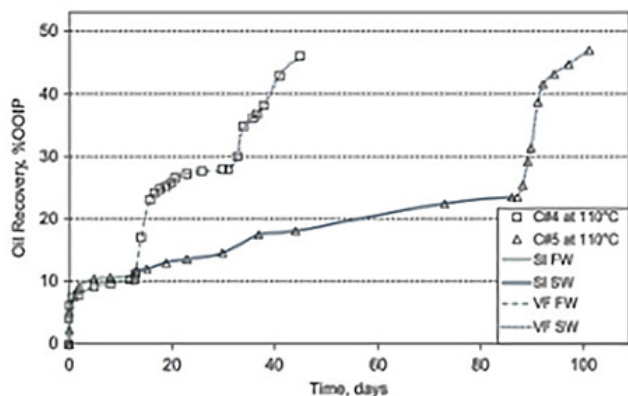


Figure 4: Effect of seawater injection on the efficiency of oil extraction, [43]

Fluid flow tests inside the core

Using the method of fluid flow inside the core, Bageci et al. in 2001 observed an increase in oil production of up to 35% of the in-situ oil was by injecting water with KCl (2% by weight of water) into the carbonate rock. They also observed an increase in the pH of the water leaving the core due to the presence of in-rock clays and ion exchange. They attributed the increase in oil production in carbonate rocks to low salinity due to the injection of water with low salinity, [44].

In 2011, Yousef et al. investigated the use of smart water injection in carbonate rocks. They used sea water at different concentrations. The results of the water flow inside the carbonate core showed that as the seawater diluted, the oil extraction efficiency increased by 18%, [45].

Gupta et al. in 2011 studied the flow of water in the cores of the Middle East limestone and the western Texas dolomite. The results showed a 5 to 9 percent increase in oil extraction efficiency for both samples due to sulfate injection. Also, according to the results, in limestone, a 7 to 9% increase in in-situ oil extraction was achieved due to a decrease in the hardness of the injected water, and an increase of 15% and 20% was observed in oil extraction efficiency in the case of application of borate and phosphate. They introduced the mechanism of change in rock wettability as a factor in increasing oil extraction in carbonate rocks [46].

Effect of ions

Effect of the concentration of Ca²⁺ ion

Figure 5 shows the effect of Ca²⁺ ion concentration on oil recovery. In the solutions where the effect of Ca²⁺ ion was investigated (PG, PG0 Ca²⁺, PG2 Ca²⁺, PG3 Ca²⁺ solutions) at temperatures below 90 °C, the oil extracted from all samples

was the same. But, at a temperature of 90 °C, with increasing Ca²⁺ ions in the solution, the extraction has also increased. However, by increasing Ca²⁺ in PG2 Ca²⁺ solution (containing 0.025 mol/L of Ca²⁺ ion) compared to PG solution (containing 0.012 mol/L of Ca²⁺ ion), identical recovery was obtained from the two solutions. In the studies conducted by Austad et al. on chalk carbonate rocks, increasing the concentration of Ca²⁺ ion in the presence of ions had a positive So₄²⁻ effect on enhanced oil recovery [47-49].

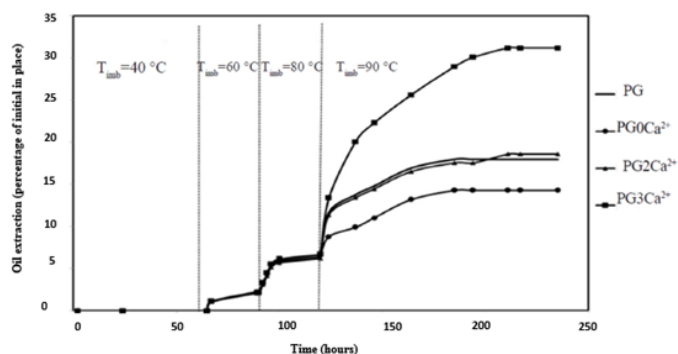


Figure 5: Effect of Ca²⁺ ion concentration on oil recovery [50]

By increasing the concentration of Ca²⁺ ion near the rock surface due to the co-adsorption of this ion in the presence of So₄²⁻ ion, the necessary ground is prepared for reaction with carboxylic substances. As a result, the separation of carboxylic materials from the surface is facilitated by the reaction of these materials with Ca²⁺ ions and the formation of complexes with these ions. Due to the change in wettability caused by the separation of carboxylic groups, self-imbibition of water and oil extraction increases [49].

Effect of So₄²⁻ ion concentration

Figure 6 shows the effect of So₄²⁻ ion concentration on oil recovery. The results of the experiments confirm that the presence of So₄²⁻ ion is very effective in increasing oil recovery. As observed in Fig. 6, the highest oil extraction in the experiments (75% OOIP) was obtained by PG3So₄²⁻ solution (containing the highest amount of So₄²⁻) and the lowest recovery (16% OOIP) has been obtained by PG0So₄²⁻ solution (without So₄²⁻ ion).

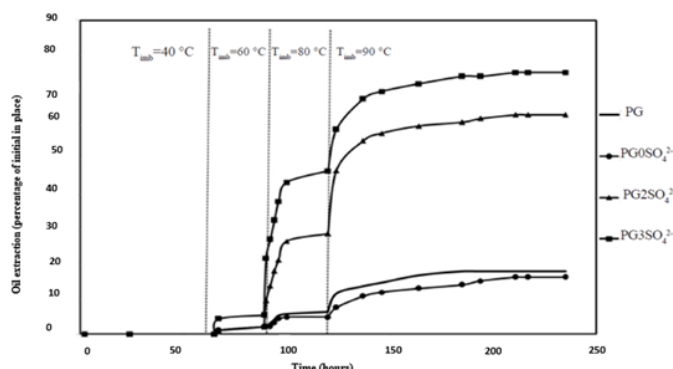


Figure 6: Effect of So₄²⁻ ion concentration on oil recovery, [50]

Researchers' studies on chalk carbonate rocks also indicate the importance of the presence of So₄²⁻ ions in changing wettability and improving self-imbibition status, [47-49]. By absorbing negatively charged So₄²⁻ ions on carbonate surfaces, the positive

charge on the surface is reduced and this issue facilitates the separation of carboxylic (negatively charged) groups from the surface, as a result of wettability of the mentioned surfaces and subsequent self-imbibition of water in the rock increase [49].

Effect of Mg²⁺ ion concentration

According to experiments performed with solutions of PG0 Mg²⁺, PG2 Mg²⁺, PG3 Mg²⁺ and PG, Mg²⁺ ions show a relatively similar behavior to Ca²⁺ ions. At 40, 60 and 80 °C, with increasing concentration of Mg²⁺ in the imbibition solution, no change was observed in oil recovery. But at 90 °C with increasing concentration of Mg²⁺ ion, the oil extraction rate also increased. While contrary to expectations, the amount of oil extracted by PG0Mg²⁺ (without Mg²⁺ ion) and PG (containing 0.073 mol/L Mg²⁺ ion) solutions was almost equal. Studies by Zhang et al. on chalk carbonate rocks show that the activity of Mg²⁺ ions is effective only at temperatures above 100 °C and, increasing the concentration of this ion at lower temperatures will not affect the oil recovery rate, [48]. However, it was predicted that due to the absence of twin water, in the initial state of saturation of 100% of the reservoir rock from oil, at temperatures below 100 °C, the effect of the presence of Mg²⁺ ions in the change of wettability is significant. Previous researchers believed that at high temperatures, Mg²⁺ would be able to separate the complex formed between Ca²⁺ ions and carboxylic groups, (Figure 7).

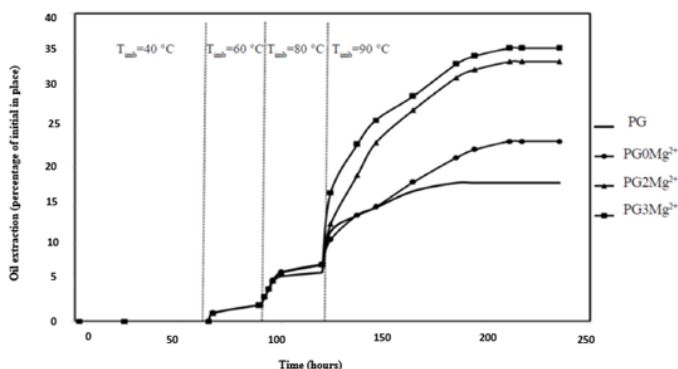


Figure 7: Effect of Mg²⁺ ion concentration on oil recovery, [50]

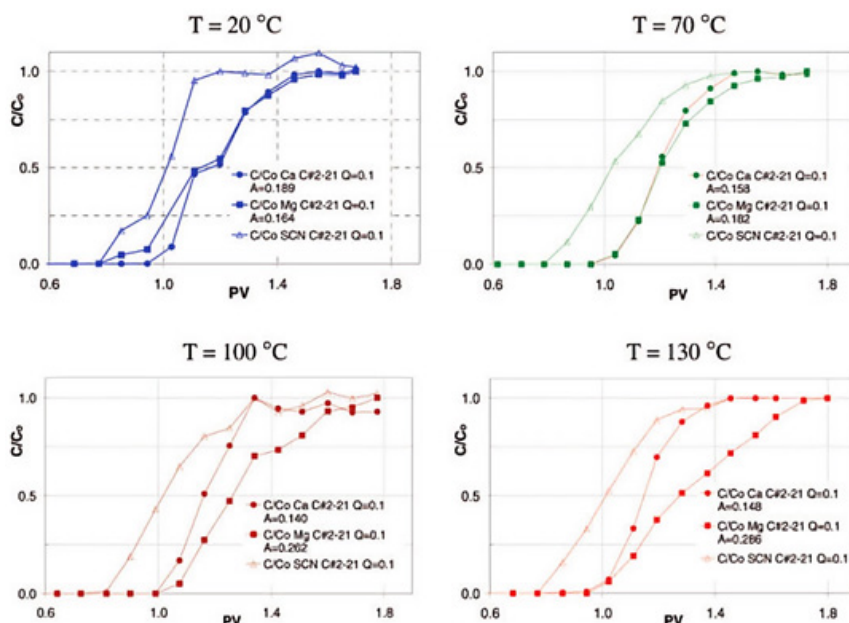


Figure 9: Effect of temperature on the competitive adsorption of ions Ca²⁺ and Mg²⁺ in sandstones, [52]

Effect of NaCl salt concentration

With decreasing the total salinity from 41.38 to 14.10 g/L due to the removal of NaCl salt concentration (TDS = 3.1 TDS (PG)), oil extraction increases by 30% at 90 °C. However, due to the addition of NaCl and increasing the total salinity to 123.23 g/L, the oil extraction rate has decreased by 2% at 90 °C. Similar results have been reported in experiments on chalk carbonate rocks by other researchers [51].

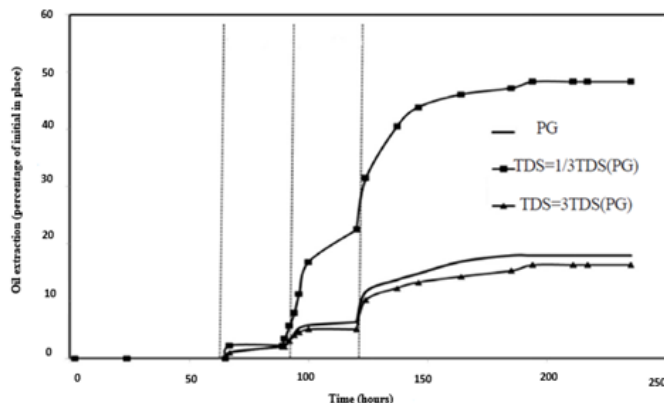


Figure 8: Effect of TDS in imbibition solution on oil recovery, [51]

Effect of temperature

Temperature is a critical parameter in most water-based enhanced oil recovery studies in chalk carbonate reservoirs. Zhang et al. investigated the adsorption of Ca²⁺ and Mg²⁺ ions with equal concentrations on the surface of carbonate chalk rock at 20 °C and 130 °C by adsorption chromatography. At 20 °C, the attraction of Ca²⁺ ion to chalk rock was higher than Mg²⁺ ion. While at 130 °C, the concentration of Ca²⁺ in the output solution was higher than its value and the concentration of Mg²⁺ ion was lower than its value in the injected fluid. The results of Fig. 9 show that the Mg²⁺ ion in the injected fluid is able to replace the Ca²⁺ ion with a 1: 1 reaction, [52].

Strand et al. investigated the effect of temperature on the competitive adsorption of Ca^{2+} and Mg^{2+} on the surface of limestone. At temperatures below 100°C , the adsorption of Ca^{2+} and Mg^{2+} towards the carbonate surface was quite similar. But with increasing temperature from 100°C to 130°C , the adsorption of Mg^{2+} is more than Ca^{2+} ion. In Fig. 10, the Ca^{2+} and Mg^{2+} curves at temperatures below 100°C are almost identical. However, with increasing temperature, the Mg^{2+} curve falls below the Ca^{2+} curve, which indicates that Mg^{2+} is more adsorbed on the limestone. At high temperatures, Mg^{2+} can replace Ca^{2+} . Fathi et al., also observed large differences in oil recovery rates between imbibition fluids (seawater, formation water, NaCl-free seawater and seawater with the concentration of 4 times NaCl concentration) at high temperatures [53].

Effect of ion concentrations in seawater on oil extraction efficiency

Puntervold et al. in 2015 investigated the effect of ion concentrations in seawater on oil extraction efficiency during self-imbibition on the chalk rock. Their results showed that with decreasing the amount of ion, the extraction efficiency increased. Fig. 10 indicates the oil extraction efficiency in self-imbibition from oil-saturated chalk rock for smart water at various concentrations of Na ions at 90°C and initial water saturation of 10% and acid number of 0.5 mg of KOH per gram.

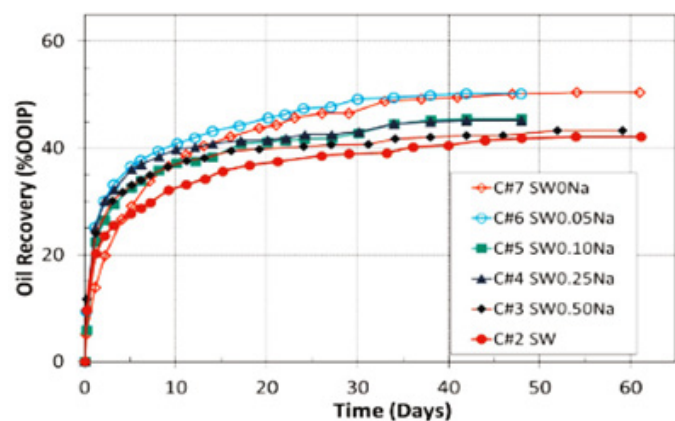


Figure 10: Oil extraction efficiency in self-imbibition from oil-saturated chalk rock for smart water at various concentrations of Na ions, [54]

According to the experimental results obtained, in order to reach higher oil extraction efficiency relative to seawater (about 8% of higher extraction efficiency), the removal of more than 90 percent of the ions in the seawater is needed [54].

Figure 11 shows the increased oil extraction efficiency by up to 10% in self-imbibition of oil-saturated chalk rock for Na ion-

free smart water at varying concentrations of So_4^{2-} ions (from 0 to 4 times the concentration in seawater) at 90°C and the initial temperature and water saturation of respectively 10% and the acid number of 0.5 mg of KOH per gram.

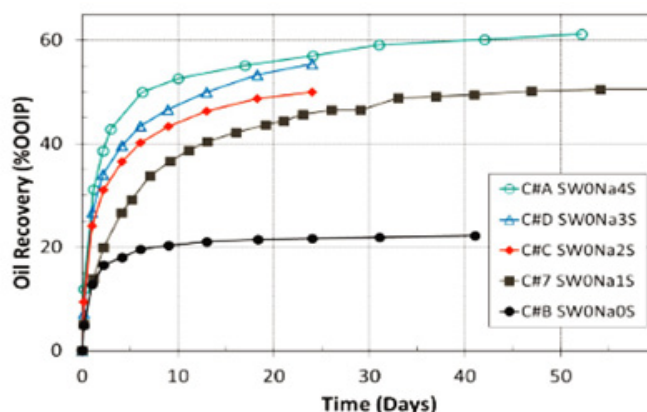


Figure 11: Increased oil extraction efficiency by up to 10% in self-imbibition of oil-saturated chalk rock for Na ion-free smart water at varying concentrations of So_4^{2-} ions, [54]

Figure 12 shows the highest oil extraction efficiency using seawater modified at different concentrations of NaCl at 90°C and an initial water saturation of 10% and an acid number of 0.5 mg KOH per gram.

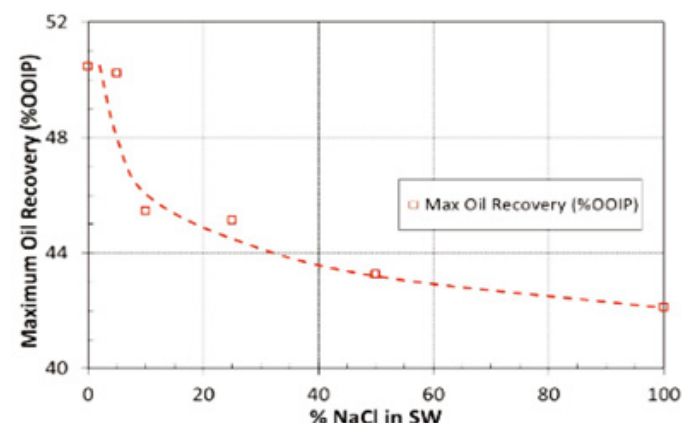


Figure 12: Highest oil extraction efficiency using seawater modified at different concentrations of NaCl, [54]

Figure 13: shows the oil extraction efficiency after 24 days of imbibition for smart water without Na ion at different concentrations of So_4^{2-} ions (from 0 to 4 times the concentration of seawater) at 90°C and initial water saturation of 10% and acid number of 0.5 mg of KOH per gram.

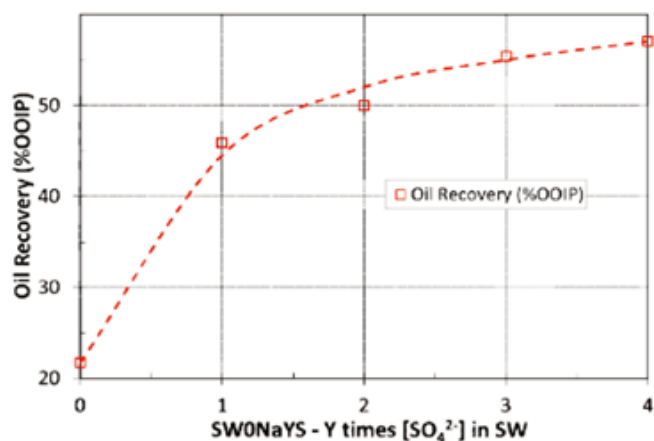


Figure 13: Oil extraction efficiency after 24 days of imbibition for smart water without Na ion at different concentrations of SO_4^{2-} ions, [54]

Interfacial tension

Examining the results of interfacial tension of water-oil systems published in previous studies, it can be seen that different numbers, trends and mechanisms have been reported, [55-57]. Compared to pure materials, the interfacial tension of crude oil is a very complex function of many parameters such as temperature, pressure, salinity and water composition, pH, acid number and type of polar materials in crude oil, [58]. As observed in previous sections of this study, the presence of water along with crude oil dissolves some polar components into the water and thus changes the properties of the water. In this section, it has been tried to investigate the effect of this phenomenon on the interfacial properties and in particular the water-oil interfacial tension through the designed experiments mentioned earlier.

First, the effect of water composition and type of ions in water on the interfacial tension of water-oil dynamics is investigated. This study can provide knowledge about the type of ion function in adsorption of polar components to the interface of two phases. Fig. 14 presents the interfacial tension of smart water designed with crude oil used. This experiment was performed using fresh oil and fresh water before the aging process.

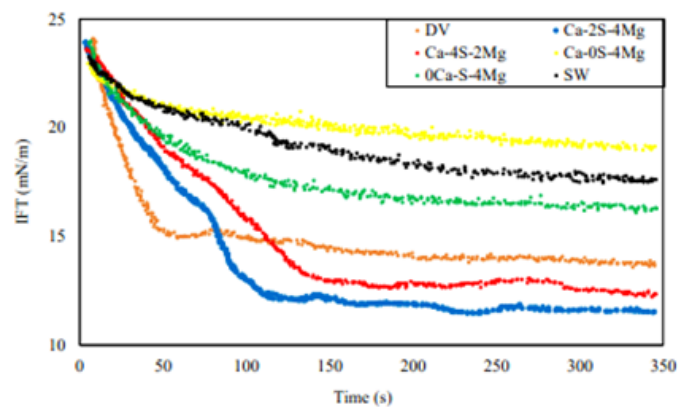


Figure 14: Interfacial tension of smart water designed with crude oil used, [59]

According to Figure 14, with increasing sulfate ions in water, the amount of equilibrium interfacial tension decreases. The lower number of equilibrium interfacial tensions indicates that more polar compounds have accumulated at the two-phase contact surface. Accordingly, the smart water with only divalent ions (DV) has also been able to rapidly pull polar oil components to the water-oil contact surface and reduce the interfacial tension. Figure 14 also shows that the presence of sulfate ions along with a cation is necessary to adsorb polar components to an interface. Due to the absence of sulfate ions in Ca-0S-4Mg water, the interfacial tension is higher than other compounds. Cations need more water molecules due to high waterproofing in the soluble mass. As a result, more molecules of water come to the mass from the surface and the asymmetric gravitational force to the mass increases and, therefore the result of interfacial tension increases. But when an anion is added to an aqueous solution, fewer water molecules are needed to waterproof the cations due to the presence of negatively charged anions. In other words, the interfacial tension will be less than that of pure cation.

Now, aware of the effect of ion type on interfacial tension, its effect on the dissolution of polar components of oil is investigated. Accordingly, the interfacial tension of aged smart water and fresh crude oil has been measured at different times of aging. Fig. 15 shows the measured interfacial tensile values of aged smart water and fresh crude oil in which the polar components are not dissolved in water.

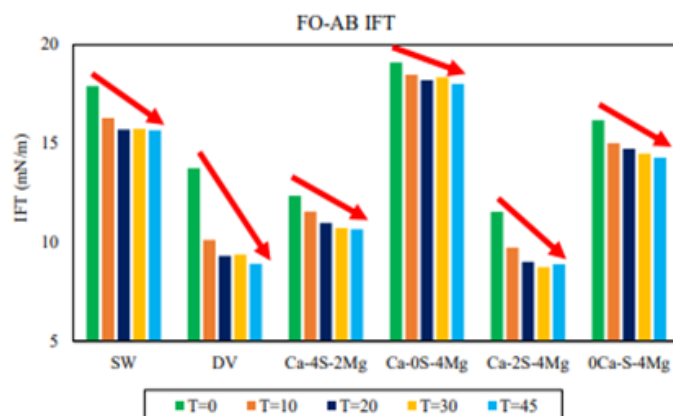


Figure 15: Measured interfacial tensile values of aged smart water and fresh crude oil, [59]

Figure 15 shows that as time passes and the dissolution of the polar components of the oil into the water increases, which decreases the pH of the water, the interfacial tension measured in all waters will decrease. Of course, the changes in interfacial tension in different waters is different. The presence of polar components and acidification of aged water has facilitated the conditions for reducing interfacial tension [59]. For more detailed investigation, Fig. 16 shows the relative variation of interfacial tension for different waters.

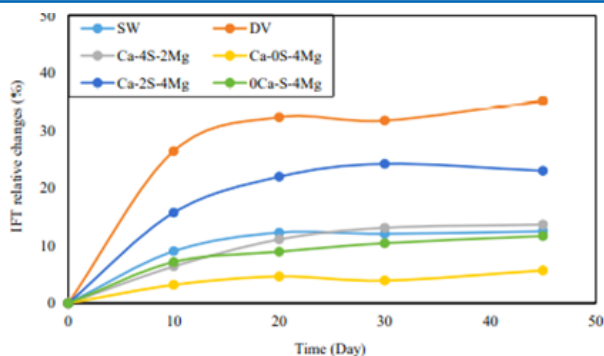


Figure 16: Relative variation of interfacial tension for different waters [59]

Figure 16 shows that the greatest change in interfacial tension occurred in DV water. If we refer to the results of pH experiments, it is clear that this water had the highest dissolution rate of polar components and the effect of this dissolution on changes in interfacial tension is also evident. Also, according to the results of dynamic interfacial tension, it was observed that the rate of adsorption of polar components on the water-oil interface by this water combination was higher than other waters. However, it seems that there is a difference between the solubility of polar components and the polarity of the surface in the adsorption of polar components to the interface of the two phases. Because DV water, which shows the highest dissolution of polar components, does not have the lowest interfacial tension compared to Ca-2S-4Mg and Ca-4S-2Mg. It can be concluded that the presence of divalent cations provides the conditions for the dissolution of polar components of oil in water and the presence of these components in the mass of water.

However, the presence of monovalent ions is essential for the accumulation of these materials on the interface of the two phases. In other words, it can be concluded that the lower concentration of polar components in the composition of Ca-2S-4Mg and Ca-4S-2Mg waters compared to DV water, therefore, is not the result of lower dissolution of polar materials. Rather, it is the result of the reabsorption of polar components dissolved in water on the interface of the two phases. To better understand the results presented, interfacial tensile tests on fresh smart water samples that have not been in contact with oil and there is no naphthenic acid and no polar component in it, and it was done using aged oil, the results of which have been presented in Figure 17.

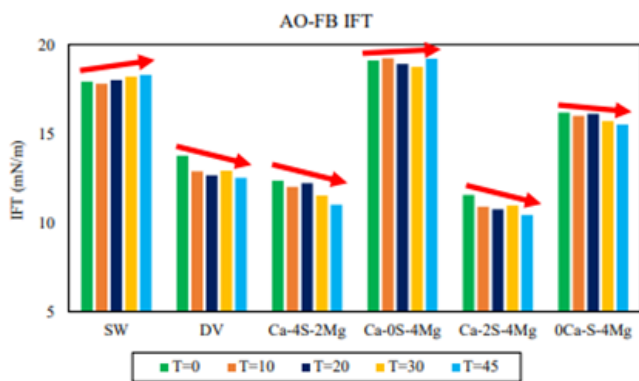


Figure 17: interfacial tension for fresh smart water samples and aged oil, [59]

According to Figure 17, the reduction in interfacial tension at different aging times shows different trends for different water compositions. Slightly increasing trend is observed for SW water, almost constant for Ca-0S-4Mg water and slight decreasing trend for the rest of the water composition. Since the aged oil has lost some of its surface activators in contact with water in this group of experiments, a reduction in interfacial tension has also been observed with a lower slope. However, waters with active divalent ions have also been able to reduce the residual amount of surface activators in the oil to the two-phase interface and reduce interfacial tension. As expected, a decreasing trend was observed in this group of experiments for interfacial tension over time and an increase in aging. However, the point is lower variation rate than the aged water- fresh oil tests. In this group of experiments, aged water has a lower pH and more polar components, but on the other hand, the amount of surface activators in aged oil is less than fresh oil. The result of these two events is that the interfacial tension in this case is more than the interfacial tension of the aged water-fresh oil system and less than the interfacial tension of the fresh water-aged oil. However, it should be noted that in all three cases where interfacial tension was measured, Ca-2S-4Mg water showed the lowest interfacial tension compared to other compounds.

Effect of dissolution on the yield of smart water injection in carbonate reservoirs

Khaksar et al. dissolved the salts at optimal concentrations with water and again measured the interfacial tension of the oil and carbonated water. The results showed that the addition of water caused a significant decrease in interfacial tension. For example, at the temperature of 75 °C and pressure of 1000 Psi, the interfacial tension has been reduced by 31% compared to the oil without salt. At the pressure of 150 Psi, 48% reduction was observed in tensile strength between water and oil. In this experiment, there is also the lowest interfacial tension between the water and oil and there will be more extraction efficiency compared to other salts. It was also observed that with increasing pressure at a certain interfacial tension temperature between the water and oil decreased which was due to the increase in solubility in water [60].

Khaksar et al. in 2017 to study the effect of water-soluble ions on the change in carbonate rock wettability by measuring the angle of contact with water in order to investigate the effect of smart water injection on carbonate rocks. They performed this experiment on several different salts. Then, the effect of changing the wettability of the rock was investigated under optimal conditions. In the first stage of their experiments, they examined the compatibility of materials with the formation water and measured the precipitation and deposition of salts in contact with the formation water to identify water-compatible salts.

Formation was observed for solutions with three salts precipitated and precipitated in water. Therefore, these salts were incompatible with formation water and were not suitable for enhanced oil extraction operations. According to their results, the use of intelligent carbonate water for injection will have a higher and more extraction efficiency than oil and changing the wettability of the rock from oil-wet to water-wet will be more effective

and the capacity to increase production related to both methods will be effective in the combined state and simultaneously and it causes the acidification of water and dissolving of rock and increases the porosity and permeability of rock, and thus increases the production of oil [61].

The results of the experiments showed that the increase in the concentration of sulfate ions had a significant effect on the oil recovery from carbonate reservoirs by the method of smart water in the self-imbibition experiment. As the ion concentration increases to three times the initial value, the oil recovery increases to about 58%. Increasing the concentration of Na⁺ ion slightly reduces the oil recovery rate. In other words, it reduces the activity of effective ions in smart water. However, a decrease in the content value of Na⁺ ion leads to a significant increase in the oil recovery. In other words, by decreasing these ions, the availability of active ions to the adsorbed fatty acid on the surface increases.

At the temperature of 51 °C, when the smart water fluids were used alone, the oil recovery from the cores was low and increasing the concentration of ions did not have much effect on increasing the yield of oil. But as the temperature rises, the oil recovery increases relative to the lower temperatures and the activity of ions in smart water solution is also increased and increasing or decreasing the concentration of ions affects the final oil recovery rate [61].

Wettability in carbonate reservoirs and its challenges

Wettability can be considered as one of the most important parameters in the oil recovery process and this is due to its very strong effect on the distribution, placement and flow of water and oil in the reservoir during production, [40]. Fluid distribution in a porous medium is not only affected by capillary, viscous, and gravitational forces, but also by forces in the solid/liquid interface. Wettability is a term used to describe the relative affinity of a surface for a fluid in the presence of other immiscible fluids. This parameter is the main factor in the microscopic distribution of the fluid in the porous medium and greatly affects the oil saturation as well as the ability of one phase to flow. This relative tendency of cavity walls to a hydrocarbon in the presence of water in the oil industry is often described by the terms water-wet and oil-wet. The strong water-wet, strong oil-wet formations with moderate wettability include Spraberry in western Texas, Bradford Black in Pennsylvania, and Fair bank sand in southern Texas, respectively. It is believed that most carbonate reservoirs have combined and oil-wet inclined wettability. It has also been shown that oil recovery for sand rock reservoirs is higher than for carbonates. The main challenge in carbonate reservoirs is the change of wettability. Wettability change is the main challenge to increase oil recovery from carbonate reservoirs. For any change in wettability, the activation energy required for chemical reactions is essential. In general, the bond energy between the polar components of oil and carbonates is higher than that found in sand rocks. Carbonate rock is neutral to oil-wet due to the adsorption of carboxylic components in crude oil on the carbonate surface. Sulfate ions alone can act as a wettability modifier without the presence of other additives such as surface activators.

The calcite surface initially adsorbs the opposite (acidic) polar components with a better acid-alkali reaction. The acidic components adsorbed on the carbonate surface include naphthalene acid and a number of carboxylic acids (RCOOHs) including caprylic (octanoic, palmitic, hexadecenoic), stearic (octadecanoic) and oleic acids. This acid-alkali interaction between oil and solid is a strong polar interaction.

New mechanism to increase oil extraction efficiency from carbonate rocks in smart water injection

Tetteh et al. in 2017 investigated the mechanisms of increasing the oil extraction from carbonate rocks in the case of applying smart water and low-salinity water. In previous work, only the main mechanism in increasing the production of carbonate rocks was the change in the wettability of the rock in contact with water. However, their results showed that in addition to this mechanism, the formation of a water-in-oil emulsion in the form of microns also did not increase the extraction efficiency. They used the core injection test. Their results showed that after injecting seawater into the core with the extraction efficiency of 40%, by injecting water with low salinity, this efficiency increases by approximately 10% to about 50%. The main mechanism in this increase in the extraction efficiency was a change in the wettability of carbonate rock [62].

However, the main point was that they did not use aged-non-carbonate rock to reduce the effect of the wettability mechanism on the oil extraction efficiency and, showed that in the case of decrease in the effect of wettability on the oil extraction efficiency, the production rate from the carbonate core increases with decreasing salinity of the injected water. Therefore, another effective mechanism, other than the change in wettability, plays a role in this increase in oil extraction efficiency, which is the same as the creation of water-in-oil microemulsions of oil.

Figure 19 shows the efficiency of oil extraction from non-aged carbonate core in the case of the injection of water formation after seawater and then injection of water with low salinity at 40 °C at a pressure of 1000Psi.

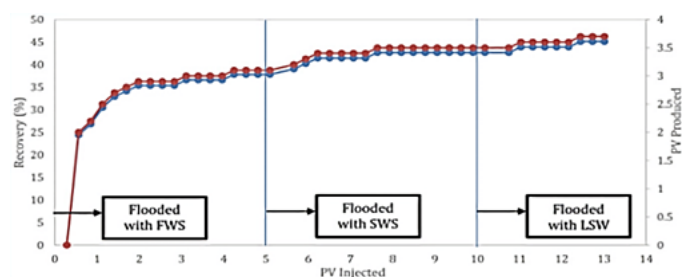


Figure 19: Efficiency of oil extraction from non-aged carbonate core, [62]

Formation of water emulsion in oil is a new mechanism to increase oil production in the case of the injection of low salinity water into oil reservoirs. Therefore, in the case of injecting water with low salinity in carbonate rocks, in addition to the mechanism of change of wettability, the mechanism of formation of micro-emulsions increases the oil extraction efficiency.

They used seawater and water formation and low-salinity water,

and several other tests were performed to prove the existence of this mechanism in the case of the injection of water with low salinity. They heated the water and oil solution by TG (thermal calorimetry) test at 600 °C. Weight loss of soluble oil was measured and evaluated with 3 water samples. According to the results, all samples had two different slopes in the graph.

Water vaporization in oil has been performed from the temperature of 80 to 350 °C and, oil components were evaporated at the temperature of more than 350 °C. Comparing the weight loss of dissolved oil with water at the temperature range of 80 to 350 °C for each of the three samples, it was found that the oil with more saline water was more stable. Because in this temperature range, the most weight loss of oil has taken place and its profile has decreased with a higher steep slope in this range [62].

Figure 20 shows the results of the TGA test for an oil and water solution at different salinities in the form of a graph of oil weight loss in terms of temperature, with a heating time of up to 2 hours.

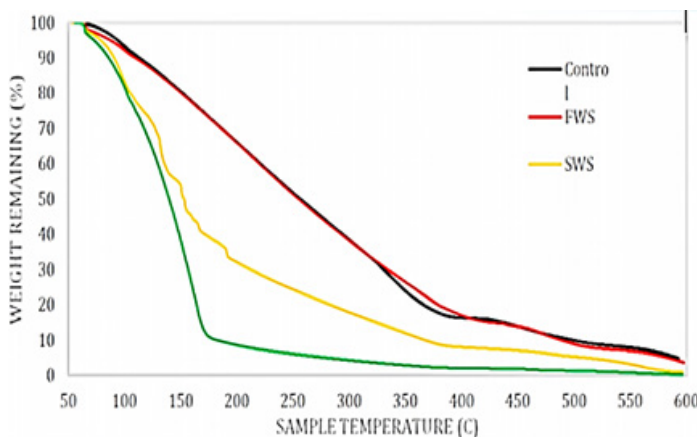


Figure 20: Results of the TGA test for an oil and water solution at different salinities [62]

They then used ESEM electron microscopes to accurately observe the oil and water solution at different salinities. According to the results of the microscope output, the microemulsions of the water scattered in the oil were clearly observed. The size of these microemulsions was about 50 microns.

Figure 21 shows the output image of the ESEM electron microscope. The shapes inside the red circles indicate the presence of microemulsions of water in the oil (for water with low salinity) with a size of 50 microns.

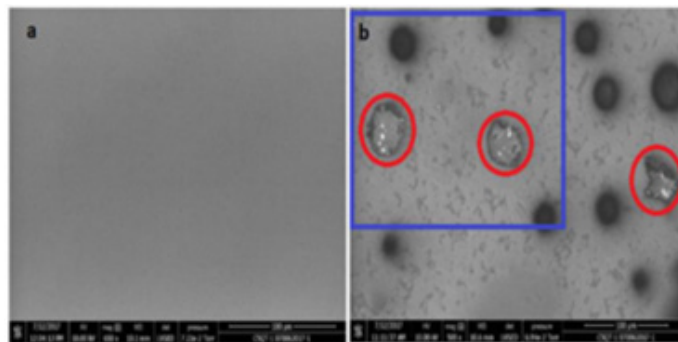


Figure 21: Output image of the ESEM electron microscope [62].

Conclusion

According to all the studies performed to investigate the stability and formation of emulsions while injecting smart water in fractured carbonate reservoirs, it can be found that:

1. With increasing ion concentration in the injected sensible water increases, the oil extraction efficiency increases. In the case of high temperature in the reservoir, this increase in extraction is more severe.
2. In case of injecting smart water as a compound, the extraction efficiency increases.
3. Smart water injection into the carbonate reservoir causes the wettability to change from oil-wet to water-wet, which causes the improved extraction efficiency.
4. In addition to the change in the wettability of the rock in contact with smart water, the formation of water emulsion in oil in microns also causes an increase in oil production. With the formation of these water-in-oil microemulsions, the oil contained in the formation will be swept in the case of smart water injection with a higher efficiency and we will have less residual oil in the rock after the water injection operation is completed.
5. The lower salinity of the injected water, the possibility of the formation of microemulsions of water in the oil increases, and the oil extraction efficiency will increase.

References

1. Austad, T., Matre, B., Milter, J., Saevaroid, A., & Øyno, L. (1998). Chemical flooding of oil reservoirs 8. Spontaneous oil expulsion from oil-and water-wet low permeable chalk material by imbibition of aqueous surfactant solutions. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 137(1-3), 117-129.
2. Strand, S., Austad, T., Puntervold, T., Høgnesen, E. J., Olsen, M., & Barstad, S. M. F. (2008). "Smart water" for oil recovery from fractured limestone: a preliminary study. *Energy & fuels*, 22(5), 3126-3133.
3. Spiecker, P. M., Gawrys, K. L., Trail, C. B., & Kilpatrick, P. K. (2003). Effects of petroleum resins on asphaltene aggregation and water-in-oil emulsion formation. *Colloids and surfaces A: Physicochemical and engineering aspects*, 220(1-3), 9-27.
4. Jones, T. J., Neustadter, E. L., & Whittingham, K. P. (1978). Water-in-crude oil emulsion stability and emulsion destabilization by chemical demulsifiers. *Journal of Canadian Petroleum Technology*, 17(02).
5. Kokal, S. L. (2005). Crude oil emulsions: A state-of-the-art review. *SPE Production & facilities*, 20(01), 5-13.
6. Mandal, A., Samanta, A., Bera, A., & Ojha, K. (2010). Characterization of oil-water emulsion and its use in enhanced oil recovery. *Industrial & Engineering Chemistry Research*, 49(24), 12756-12761.
7. Zhang, T., Davidson, A., Bryant, S. L., & Huh, C. (2010, April). Nanoparticle-stabilized emulsions for applications in enhanced oil recovery. In *SPE improved oil recovery symposium*. OnePetro.
8. Kim, I., Worthen, A. J., Johnston, K. P., DiCarlo, D. A., & Huh, C. (2016). Size-dependent properties of silica nanoparticles for Pickering stabilization of emulsions and foams. *Journal of Nanoparticle Research*, 18(4), 1-12.
9. Qiao, P., Harbottle, D., Tchoukov, P., Masliyah, J., Sjoblom, J., Liu, Q., & Xu, Z. (2017). Fractionation of asphaltenes in understanding their role in petroleum emulsion stability and

- fouling. *Energy & Fuels*, 31(4), 3330-3337.
10. Umar, A. A., Negash, B. M., Saaid, I. M., Sulaimon, A. A., Shahpin, H. B., & Mohamed, A. S. (2017, November). Effects of selected process variables on the stability of petroleum emulsions co-stabilized by carbon black and surfactant. In *SPE Symposium: Production Enhancement and Cost Optimisation*. OnePetro.
 11. Sharma, T., Kumar, G. S., Chon, B. H., & Sangwai, J. S. (2015). Thermal stability of oil-in-water Pickering emulsion in the presence of nanoparticle, surfactant, and polymer. *Journal of Industrial and Engineering Chemistry*, 22, 324-334.
 12. Piroozian, A., Hemmati, M., Ismail, I., Manan, M. A., Bayat, A. E., & Mohsin, R. (2016). Effect of emulsified water on the wax appearance temperature of water-in-waxy-crude-oil emulsions. *Thermochemica Acta*, 637, 132-142.
 13. Huang, Q., Mao, F., Han, X., Yan, J., & Chi, Y. (2014). Characterization of emulsified water in petroleum sludge. *Fuel*, 118, 214-219.
 14. Hunter, T. N., Pugh, R. J., Franks, G. V., & Jameson, G. J. (2008). The role of particles in stabilising foams and emulsions. *Advances in colloid and interface science*, 137(2), 57-81.
 15. Maaref, S., Ayatollahi, S., Rezaei, N., & Masihi, M. (2017). The effect of dispersed phase salinity on water-in-oil emulsion flow performance: a micromodel study. *Industrial & Engineering Chemistry Research*, 56(15), 4549-4561.
 16. Maaref, S., & Ayatollahi, S. (2018). The effect of brine salinity on water-in-oil emulsion stability through droplet size distribution analysis: a case study. *Journal of Dispersion Science and Technology*, 39(5), 721-733.
 17. Subramanian, D., May, N., & Firoozabadi, A. (2017). Functional molecules and the stability of water-in-crude oil emulsions. *Energy & Fuels*, 31(9), 8967-8977.
 18. Yu, L., Sang, Q., Dong, M., & Yuan, Y. (2017). Effects of interfacial tension and droplet size on the plugging performance of oil-in-water emulsions in porous media. *Industrial & Engineering Chemistry Research*, 56(32), 9237-9246.
 19. Sun, M., Mogensen, K., Bennetzen, M., & Firoozabadi, A. (2016). Demulsifier in injected water for improved recovery of crudes that form water/oil emulsions. *SPE Reservoir Evaluation & Engineering*, 19(04), 664-672.
 20. Yarranton, H. W., Hussein, H., & Masliyah, J. H. (2000). Water-in-hydrocarbon emulsions stabilized by asphaltenes at low concentrations. *Journal of colloid and interface science*, 228(1), 52-63.
 21. Silva, F. L. M. C., Tavares, F. W., & Cardoso, M. J. E. M. (2013). Thermodynamic stability of water-in-oil emulsions. *Brazilian Journal of Petroleum and Gas*, 7(1).
 22. Gafonova, O. V., & Yarranton, H. W. (2001). The stabilization of water-in-hydrocarbon emulsions by asphaltenes and resins. *Journal of Colloid and Interface Science*, 241(2), 469-478.
 23. Poteau, S., Argillier, J. F., Langevin, D., Pincet, F., & Perez, E. (2005). Influence of pH on stability and dynamic properties of asphaltenes and other amphiphilic molecules at the oil-water interface. *Energy & Fuels*, 19(4), 1337-1341.
 24. Dicharry, C., Arla, D., Siquin, A., Graciaa, A., & Bouriat, P. (2006). Stability of water/crude oil emulsions based on interfacial dilatational rheology. *Journal of colloid and interface science*, 297(2), 785-791.
 25. Qiao, P., Harbottle, D., Tchoukov, P., Wang, X., & Xu, Z. (2017). Asphaltene Subfractions Responsible for Stabilizing Water-in-Crude Oil Emulsions. Part 3. Effect of Solvent Aromaticity. *Energy & Fuels*, 31(9), 9179-9187.
 26. McGurn, M. (2017). *Emulsion Layer Growth in Asphaltene/Solids-Stabilized Water-in-Oil Emulsions* (Master's thesis, Graduate Studies).
 27. Eshraghi, S. E., Kazemzadeh, Y., Etemadan, Z., & Papi, A. (2018). Detecting high-potential conditions of asphaltene precipitation in oil reservoir. *Journal of Dispersion Science and Technology*, 39(7), 943-951.
 28. Parsaei, R., Kazemzadeh, Y., Abadshapoori, A. K., & Riazi, M. (2017, June). Study of asphaltene precipitation during CO₂ injection to oil reservoirs in the presence of iron oxide nanoparticles by interfacial tension and bond number measurements. In *79th EAGE Conference and Exhibition 2017* (Vol. 2017, No. 1, pp. 1-1). European Association of Geoscientists & Engineers.
 29. Doryani, H., Kazemzadeh, Y., Parsaei, R., Malayeri, M. R., & Riazi, M. (2015). Impact of asphaltene and normal paraffins on methane-synthetic oil interfacial tension: An experimental study. *Journal of Natural Gas Science and Engineering*, 26, 538-548.
 30. Kazemzadeh, Y., Parsaei, R., & Riazi, M. (2015). Experimental study of asphaltene precipitation prediction during gas injection to oil reservoirs by interfacial tension measurement. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 466, 138-146.
 31. Kazemzadeh, Y., Malayeri, M. R., Riazi, M., & Parsaei, R. (2015). Impact of Fe₃O₄ nanoparticles on asphaltene precipitation during CO₂ injection. *Journal of Natural Gas Science and Engineering*, 22, 227-234.
 32. Joonaki, E., Youzband, A. H., Burgass, R., & Tohidi, B. (2017, June). Effect of water chemistry on asphaltene stabilised water in oil emulsions-A new search for low salinity water injection mechanism. In *79th EAGE Conference and Exhibition 2017* (Vol. 2017, No. 1, pp. 1-5). European Association of Geoscientists & Engineers.
 33. Zorzenão, P. C., Mariath, R. M., Pinto, F. E., Tose, L. V., Romao, W., Santos, A. F., ... & Yamamoto, C. I. (2018). Asphaltene subfractions extracted from Brazilian vacuum residue: Chemical characterization and stabilization of model water-in-oil (W/O) emulsions. *Journal of Petroleum Science and Engineering*, 160, 1-11.
 34. Bourrel, M., & Passade-Boupat, N. (2017). Crude oil surface active species: Consequences for enhanced oil recovery and emulsion stability. *Energy & Fuels*, 32(3), 2642-2652.
 35. Qiao, P., Harbottle, D., Tchoukov, P., Masliyah, J., Sjoblom, J., Liu, Q., & Xu, Z. (2017). Fractionation of asphaltenes in understanding their role in petroleum emulsion stability and fouling. *Energy & Fuels*, 31(4), 3330-3337.
 36. Duan, M., Song, X., Zhao, S., Fang, S., Wang, F., Zhong, C., & Luo, Z. (2017). Layer-by-layer assembled film of asphaltene/polyacrylamide and its stability of water-in-oil emulsions: a combined experimental and simulation study. *The Journal of Physical Chemistry C*, 121(8), 4332-4342.
 37. Salehi, M., Johnson, S. J., & Liang, J. T. (2008). Mechanistic study of wettability alteration using surfactants with applications in naturally fractured reservoirs. *Langmuir*, 24(24), 14099-14107.
 38. Zhang, P., Tweheyo, M. T., & Austad, T. (2006). Wettability alteration and improved oil recovery in chalk: The effect of calcium in the presence of sulfate. *Energy & Fuels*, 20(5), 2056-2062.
 39. Lashkarbolooki, M., Ayatollahi, S., & Riazi, M. (2014). The impacts of aqueous ions on interfacial tension and wettability of an asphaltene-acidic crude oil reservoir during smart water injection. *Journal of Chemical & Engineering Data*, 59(11), 3624-3634.

40. Anderson, W. G. (1986). Wettability literature survey-part 1: rock/oil/brine interactions and the effects of core handling on wettability. *Journal of petroleum technology*, 38(10), 1125-1144.
41. Webb, K. J., Black, C. J. J., & Tjetland, G. (2005, November). A laboratory study investigating methods for improving oil recovery in carbonates. In *International petroleum technology conference*. OnePetro.
42. Zhang, P., Tweheyo, M. T., & Austad, T. (2007). Wettability alteration and improved oil recovery by spontaneous imbibition of seawater into chalk: Impact of the potential determining ions Ca^{2+} , Mg^{2+} , and SO_4^{2-} . *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 301(1-3), 199-208.
43. Strand, S., Puntervold, T., & Austad, T. (2008). Effect of temperature on enhanced oil recovery from mixed-wet chalk cores by spontaneous imbibition and forced displacement using seawater. *Energy & Fuels*, 22(5), 3222-3225.
44. S. Bagci, M.V. Kok, U. Turksoy (2001) "Effect of brine composition on oil recovery by water flooding", *Journal of Petroleum Science and Technology*, 19(34), 359-372.
45. Yousef, A. A., Al-Saleh, S., Al-Kaabi, A., & Al-Jawfi, M. (2011). Laboratory investigation of the impact of injection-water salinity and ionic content on oil recovery from carbonate reservoirs. *SPE Reservoir Evaluation & Engineering*, 14(05), 578-593.
46. Gupta, R., Smith, P. G., Hu, L., Willingham, T. W., Cascio, M. L., Shyeh, J. J., & Harris, C. R. (2011, September). Enhanced waterflood for middle east carbonate cores—impact of injection water composition. In *SPE Middle East oil and gas show and conference*. OnePetro.
47. Zhang, P., & Austad, T. (2006). Wettability and oil recovery from carbonates: Effects of temperature and potential determining ions. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 279(1-3), 179-187.
48. Zhang, P., Tweheyo, M. T., & Austad, T. (2007). Wettability alteration and improved oil recovery by spontaneous imbibition of seawater into chalk: Impact of the potential determining ions Ca^{2+} , Mg^{2+} , and SO_4^{2-} . *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 301(1-3), 199-208.
49. Strand, S., Høgenesen, E. J., & Austad, T. (2006). Wettability alteration of carbonates—Effects of potential determining ions (Ca^{2+} and SO_4^{2-}) and temperature. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 275(1-3), 1-10.
50. H. Sadeghi Marznaki, S.N.A. Ashrafizadeh (2013) "Investigation of the effect of effective ions on surface potential in improving oil extraction by Spontaneous Imbibition process (In persian)", *Petroleum Research*, 71, 3-13.
51. Fathi, S. J., Austad, T., & Strand, S. (2010). "Smart water" as a wettability modifier in chalk: the effect of salinity and ionic composition. *Energy & fuels*, 24(4), 2514-2519.
52. Zhang, P., Tweheyo, M. T., & Austad, T. (2007). Wettability alteration and improved oil recovery by spontaneous imbibition of seawater into chalk: Impact of the potential determining ions Ca^{2+} , Mg^{2+} , and SO_4^{2-} . *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 301(1-3), 199-208.
53. Fathi, S. J., Austad, T., & Strand, S. (2011). Water-based enhanced oil recovery (EOR) by "smart water": Optimal ionic composition for EOR in carbonates. *Energy & fuels*, 25(11), 5173-5179.
54. Puntervold, T., Strand, S., Ellouz, R., & Austad, T. (2015). Modified seawater as a smart EOR fluid in chalk. *Journal of Petroleum Science and Engineering*, 133, 440-443.
55. Lashkarbolooki, M., Riazi, M., Ayatollahi, S., & Hezave, A. Z. (2016). Synergy effects of ions, resin, and asphaltene on interfacial tension of acidic crude oil and low-high salinity brines. *Fuel*, 165, 75-85.
56. Bai, J. M., Fan, W. Y., Nan, G. Z., Li, S. P., & Yu, B. S. (2010). Influence of interaction between heavy oil components and petroleum sulfonate on the oil-water interfacial tension. *Journal of dispersion science and technology*, 31(4), 551-556.
57. Lashkarbolooki, M., Ayatollahi, S., & Riazi, M. (2014). Effect of salinity, resin, and asphaltene on the surface properties of acidic crude oil/smart water/rock system. *Energy & fuels*, 28(11), 6820-6829.
58. Buckley, J. S., & Fan, T. (2007). Crude oil/brine interfacial tensions 1. *Petrophysics-The SPWLA Journal of Formation Evaluation and Reservoir Description*, 48(03).
59. R. Mokhtari, S.S. Ayatollahi (2018) "Laboratory study of the effects of divalent intelligent water ions on the surface interactions of the water-crude oil system (In Persian)", *J. Of Applied Chemistry*, 30(43), 147-163.
60. Manshad, A. K., Olad, M., Taghipour, S. A., Nowrouzi, I., & Mohammadi, A. H. (2016). Effects of water soluble ions on interfacial tension (IFT) between oil and brine in smart and carbonated smart water injection process in oil reservoirs. *Journal of Molecular Liquids*, 223, 987-993.
61. Manshad, A. K., Nowrouzi, I., & Mohammadi, A. H. (2017). Effects of water soluble ions on wettability alteration and contact angle in smart and carbonated smart water injection process in oil reservoirs. *Journal of Molecular Liquids*, 244, 440-452.
62. Tetteh, J. T., Rankey, E., & Barati, R. (2017, October). Low salinity waterflooding effect: Crude oil/brine interactions as a recovery mechanism in carbonate rocks. In *OTC Brasil*. OnePetro.

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