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A Review of Wettability Alteration by Spontaneous Imbibition Using Low-Salinity Water in Naturally Fractured Reservoirs

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Abstract: Analysis of fluid flow in naturally fractured reservoirs (NFRs), as a highly heterogeneous and complex system, requires a detailed study of the fracture-matrix interactions. The main process of fluid movement between the fracture and matrix is spontaneous imbibition (SI), which can occur in co/countercurrent fluid flow states. In addition, most carbonate rocks are fractured and non-water-wet, which can lead to low oil recovery. Wettability greatly affects the performance of the SI process. Injection of water or chemicals can be insufficient because fluids mostly pass through highly permeable fractures and lead to early breakthrough. Therefore, the wettability alteration mechanism should be applied in NFRs, and low-salinity water (LSW) injection is considered an effective enhanced oil recovery (EOR) approach. In this review, experimental and numerical studies of co/countercurrent imbibition are analyzed to show the importance of investigating the fracture-matrix interactions. In addition, the review shows the wettability effect on imbibition in fractured rocks. The review of experimental studies of LSW imbibition in fractured carbonates shows the possibilities for implementing an EOR method. However, the wettability alteration process during SI using LSW has not yet been studied, and no simulation models of co/countercurrent flows have yet been provided. Based on this review, more experimental studies are recommended to duplicate co/countercurrent imbibition using LSW. Advanced techniques such as CT scanning, MRI, and NTI can be used to reveal fluid distribution. Using experimental data, numerical models can be developed to characterize dynamic wettability alteration during co/countercurrent imbibition.



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1. Introduction

NFRs contain significant hydrocarbon reserves. These reservoirs consist of two systems: a matrix with low permeability surrounded by fractures with high conductivity [1–4]. The term “fracture” is defined as a mechanical discontinuity formed by brittle deformation of the Earth’s stress field [5]. The fracture’s aperture, height, and length describe its transport of fluid as a conduit. Fractures can increase permeability and affect well productivity, but reservoir development of NFRs is a difficult and complex process. A fracture is also defined from its fluid movement ability as a heterogeneous zone with high permeability surrounded by a low permeability matrix [4]. The NFR has channels that hold most of the injected fluid and a matrix that keeps oil inside because of the higher pore volume and porosity compared to the fractures [3,4]. The oil recovery is usually low in NFRs because of the extreme heterogeneity caused by natural fractures.

Waterflooding is one of the most common secondary recovery methods. For NFRs, standalone waterflooding cannot be effective due to water channeling caused by the conductive path of fractures, leading to early water breakthrough. In addition, most fractured carbonates have unfavorable wettability, which decreases the oil production from the matrix. Hence, EOR methods such as engineered water (EW) flooding, LSW flooding, or combined methods with chemicals such as surfactants, alkalis, polymers, and nanoparticles are applied to alter the wettability toward water-wetness and increase oil production [6].

Recently, the use of these chemical methods has gained a lot of interest for wettability alteration, though the major limitation of these chemical wettability modifiers is the cost. LSW injection is more practical than other injection methods due to its availability and environmental compatibility. LSW can be prepared by diluting formation brine and, in some cases, by adjusting potential determining ions (PDIs) in the diluted water. This prepared water is also called smart water [7–9]. The presence of PDIs is critical to improving the performance of the EW to alter rock wettability [10].

In addition, the application of LSW or smart water with chemicals is proposed as an effective hybrid EOR method. LSW injection can be applied with a combination of surfactants [11,12], the polymer [13,14], and more novel chemicals such as nanoparticles [15,16]. LSW injection can also be optimized to decrease the operational cost of preparing LSW or smart water [17,18].

The effect of LSW flooding was first discovered in sandstone. The processes of LSW in carbonates differ from sandstone because of its mineral composition. Hence, the application of LSW flooding in carbonates has only more recently been analyzed and is not yet well investigated [19,20]. In addition, natural fractures complicate the processes of LSW injection due to their nature and heterogeneity. The following mechanisms are proposed in the literature as the reasons behind the incremental oil recovery due to LSW flooding in carbonates and sandstone.

1.1. Mineral Dissolution

Calcite dissolution was suggested as the prime mechanism for wettability alteration in carbonates during LSW injection [21,22]. When the injected LSW contains more SO_4^{2-} ions than formation water in the reservoir, the earlier equilibrium between the carbonate rock, formation water, and crude oil is disturbed, leading to an increase in the precipitation of anhydrite (CaSO_4). This causes the loss of the Ca^{2+} concentration in the aqueous phase. The dissolution of calcite occurs to compensate for the lack of Ca^{2+} ions and reach chemical equilibrium. If the dissolution of calcite occurs in the areas where the oil molecules adsorb, the oil molecules will be liberated from the rock surface [23,24]. Calcite dissolution can also lead to the enlargement of the pore sizes, as well as enhance the connectivity between the micro- and macropores [25,26]. On the contrary, authors [27,28] suggested that rock dissolution is not responsible for wettability alteration during LSW injection in carbonates. They further proposed that rock dissolution is only relevant in the laboratory and not at the reservoir scale.

1.2. pH Increase and In Situ Surfactant Generation

Due to the oil carboxylic group complex with cations such as Ca^{2+} , the concentration of calcium ions reduces, and calcite dissolution occurs. Calcite dissolution in the reservoir causes hydrogen removal and this can increase pH [29,30]. When the pH of the solution is higher than the point of zero charge, a change will occur in the rock surface charge. Consequently, double-layer expansion occurs and will eventually lead to wettability alteration [31]. Meanwhile, pH increase is followed by generating in situ surfactant from carboxylic compounds of oil, and a type of alkaline flood occurs that can lower the IFT [32–34].

1.3. Electric Double Layer (EDL) Expansion

The authors of [35] suggested that the wettability alteration of carbonates is directly linked to the influence of the variation in the EDL, which refers to the bulk of the ions that are close to the surface, formed due to the interaction between the charged rock surface and brine. The distribution of charges at the surface is composed of opposite charges (counter-ions) attracted to the surface and other equal charges (co-ions) repulsed from the surface in an aqueous medium. Due to this charge accumulation, an electrical layer is formed [36–39].

During LSW in carbonate rocks, the surface tends to be less positive due to the ionic exchange between cations in aqueous brine and calcium ions. The substitution of calcium ions with the aid of a solvation process results in the detachment of adsorbed oil. This leads to double-layer expansion and ultimately results in the wettability alteration (i.e., more water-wet) of the rock surface [40]. On the other hand, as the ionic strength of the bulk solution decreases, the thickness of the two EDLs at the oil/brine and brine/rock interfaces increases. EDL expansion leads to an increase in repulsion forces between rock and oil interfaces. Hence, the brine film between the oil and rock surface becomes more stable, which results in more oil detachment from the surface [41].

1.4. Multicomponent Ionic Exchange (MIE)

The authors of [42] proposed this mechanism as the main driver for wettability alteration in carbonates for LSW. The PDIs must be present in the injection brine for MIE to occur [18,43]. MIE involves the adsorption of sulfate ions present in the injected water on the positively charged surface of the carbonates so that the initial positive charge of the surface reduces. This leads to the adherence of potential determining cations to the rock surface due to the lower electrostatic repulsion. At the oil-wet surface of the rock, calcium and magnesium react with the adsorbed surface-active components from the oleic phase, releasing some of them and, in turn, diminishing the oil-wet nature of the rock surface [31,33,44–46].

1.5. Salting-In

This mechanism was proposed by authors of [47,48] as a result of rock dissolution. A lower salt concentration increases the solubility of carboxylic groups. Active ions with negative charges tend to be attracted to the positive calcite surface and substitute the calcium ions, which are bonded to the negative molecules of carboxylates. Hence, the surface becomes less oil-wet as the divalent ions move from the rock surface toward the brine.

1.6. Formation of Microdispersion

This mechanism is considered a fluid-fluid interaction mechanism that can improve oil recovery by making the rock more water-wet and by swelling the oil phase. In addition, it can block highly permeable zones and transfer injected brine to unswept zones. Although all researchers agree that the formation of these microdispersions can improve sweep efficiency during LSW flooding, the mechanistic role of microdispersions is still unclear. Some researchers [20,49] proposed that water-in-oil microdispersions were formed because of natural surface-active agents in crude oil. At a low-salinity brine–oil interface, the intermolecular forces holding the oil–brine interface rigid become weak because of the low ionic strength. Water molecules then easily move into the oil phase to interact with the surface-active agents, forming reverse micelles referred to as water-in-oil microdispersions [50–55]. They are formed because of the osmotic movement as a result of the injected LSW and HSW connate water [56].

1.7. Osmosis Pressure Effect

This mechanism was suggested by authors of [57]. The osmosis effect causes connate water expansion and movement of the unswept oil, resulting in increased oil production [56,58]. However, [59] showed that this is not the primary mechanism of LSW flooding.

Wettability alteration is the main and most acceptable mechanism for the incremental oil recovery achieved in carbonate rocks with the use of LSW. Even though many attempts have been made to explain the underlying mechanisms that cause wettability alteration, there is still no general agreement about the dominant mechanism [60]. The authors of [61] believe that changing the rock surface charge through MIE is the primary mechanism of LSW, while dissolution is a secondary mechanism consistent with field-scale observations. Meanwhile, the authors of [27,62] propose that mineral dissolution could be the dominant

mechanism of LSW, while the authors of [63] suggest that both mineral dissolution and surface charge change may make up the underlying mechanism of LSW. In our recent experimental work, to be published soon, the dominant mechanisms are calcite dissolution and a pH increase alkali effect. According to the mentioned studies, the LSW effect and relative importance of the different wettability alteration mechanisms depend on rock mineralogy, brine composition and salinity, pH, temperature, and other experimental conditions. However, in most of the works, mineral dissolution and surface charge change through MIE theory are considered to make up the dominant mechanism for change of the wettability toward more water-wet states.

Table 1 shows the field implementation and macroscale investigation of LSW in sandstone and carbonates. It can be noted that there are no examples of LSW application in NFRs and only a few in carbonate reservoirs. This can be explained by noting that fractured reservoirs have a complex geology and the mechanisms of LSW are not well investigated in fractured carbonates. Hence, more studies at a small scale are still required to design LSW flooding at the field scale for NFRs.

Table 1. LSW field implementation.

Country	Reservoir	Reservoir Conditions	Rock Type	Injected Brine/Formation Brine (ppm)	pH Value	Injected Brine Volume	Type of Waterflood	Results	Author(s)
USA	–	–	Sandstone	3000/220,000	–	–	Log-inject-log	25–50 % reduction in S_{or}	[64]
USA	Alaska North Slope	$T = 155\text{ }^{\circ}\text{F}$	Sandstone	150–1500/15,000	pH increase from ~7.7 to 10.5	–	SWCTT (single well chemical tracer test)	6–12% incremental oil recovery; LSW at 7000 ppm showed no increase in oil recovery	[32]
USA	West Semlek Reservoir North Semlek Reservoir Moran Reservoir	$P_i = 2847\text{ psi}$, $T = 144\text{ }^{\circ}\text{F}$ $P_i = 2700\text{ psi}$, $T = 140\text{ }^{\circ}\text{F}$ $P_i = 4381\text{ psi}$, $T = 200\text{ }^{\circ}\text{F}$	Sandstone	10,000/60,000 3304/42,000 7948/128,000	–	~0.75 PV ~0.38 PV ~0.3 PV	Field pilot	LSW showed higher oil recovery	[65]
–	–	$P_i = 2300\text{ psi}$, $T = 181\text{ }^{\circ}\text{F}$	Sandstone	2650/15,000	–	–	SWCTT	10–15% residual oil saturation	[66]
Syria	Omar Oil Field, Isa Oil Field	–	Sandstone $\phi = 10\text{--}15\%$	2200/90,000	–	~0.6 PV	Field	10–15% incremental oil recovery	[67]
USA	Endicott Oil Field	–	Sandstone $\phi = 20\%$ $k = 100\text{ mD}$	12,000/–	–	1.3 PV	Pilot test	13% incremental oil recovery	[68]
Norway	Snorre Field	–	Sandstone $\phi = 14\text{--}32\%$ $k = 100\text{ mD--}4\text{ D}$	440/36,900	pH of FW = 7 pH of injected seawater = 7.4 pH of produced water = 6.6–7.7	–	SWCTT	No significant change; the initial wettability condition was probably sufficient for efficient production	[69]
Saudi Arabia	–	–	Carbonate	–	–	–	SWCTT	Reduction by 7 units of residual oil saturation	[26]
West Africa	–	$T = 190\text{ }^{\circ}\text{F}$	Sandstone	200/27,000–87,000	–	1.5 PV	SWCTT	Low S_{or} reduction	[70]
Russia	Zichebashkoe Field Bastrykskoye Field	$P_i = 1740\text{ psi}$, $T = 77\text{ }^{\circ}\text{F}$ $P_i = 1653\text{ psi}$, $T = 77\text{ }^{\circ}\text{F}$	Sandstone	848/248,529 848/239,393	–	–	7 years of LSW injection 13 years of LSW injection	1% incremental oil recovery	[71]
Russia	Pervomaiskoye Field	$P_i = 2407\text{ psi}$, $T = 86\text{ }^{\circ}\text{F}$	Sandstone $\phi = 17\text{--}20\%$ $k = 97\text{ mD--}432\text{ mD}$	848/252,738	pH of HSW = 6.5 pH of LSW = 7.5	~0.6 PV	7 pilot tests	Water cut decreased from 87% to 80% 5–9% incremental RF	[72]
Kuwait	Greater Burgan Field	$P_i = 2100\text{ psi}$, $T = 129\text{--}135\text{ }^{\circ}\text{F}$	Sandstone $\phi = 10\text{--}25\%$ $k = 1000\text{ mD--}5000\text{ mD}$	700/148,000	–	2 PV	SWCTT	3% reduction in S_{or}	[73]
Africa	Belayim Field	$T = 169\text{--}181\text{ }^{\circ}\text{F}$	Sandstone $\phi = 21\%$ $k = 237\text{--}464\text{ mD}$	3000–5300/220,000	–	–	SWCTT	Reduction of 5–11 saturation units	[74]
UAE	–	–	Carbonate	241/204,201	–	–	SWCTT	Planning to conduct	[75]

In the following sections, the SI process in NFRs is explained in more detail because it is considered the main mechanism of fluid movement between fracture and matrix. Experimental studies of the core scale range are described to show the difference between co- and countercurrent imbibition. Experimental and numerical investigations of the wettability effect on co/countercurrent imbibition are also reviewed. LSW as a wettability modifier is explained and experimental and simulation studies are described to show the effectiveness of LSW injection in NFRs. Section 2 reveals the difference between forced and spontaneous imbibition, emphasizing the SI process as the main driving force in NFRs.

The effect of gravity is discussed in advance as it can require conducting experimental work on co/countercurrent imbibition. Matrix wettability is also an important parameter that affects the recovery performance of NFRs. The non-water wet state can result in a low-SI process, which is the main topic of this review. Section 3 presents basic experimental methods for measuring the SI process and applying different boundary conditions to duplicate the matrix-fracture interaction. Section 4 considers the main experimental works to evaluate LSW spontaneous imbibition and the application of LSW in NFRs. Section 5 explains numerical studies conducted to model LSW in NFRs. It shows the basic approach to modeling LSW through the application of geochemical equations, shifting relative permeability, and capillary pressure curves. Section 6 describes the SI process in NFRs through analytical equations, and further developments in numerical studies are applied to integrate the wettability alteration process into analytical equations. The application of LSW in NFRs can increase oil production by altering the matrix wettability. However, detailed experimental and simulation works should be conducted to evaluate the matrix-fracture interaction during SI of LSW.

2. Fluid Flow Processes in NFR

2.1. Forced and Spontaneous Imbibition

Waterflooding is considered a secondary oil recovery method in which water displaces oil because of gravity, viscous, and capillary forces. However, most oil accumulates in the matrix in a fractured reservoir, and oil production is caused by capillary forces and spontaneous water imbibition into the matrix. Imbibition is defined as a process in which the saturation of the wetting phase increases while the saturation of the non-wetting phase decreases. Most of the injected water goes through highly permeable fractures and leads to low sweep efficiency [76]. Therefore, one of the main mechanisms of production in NFRs is SI, which causes secondary hydrocarbon production [3]. Imbibition is divided into two types: spontaneous and forced. Commonly, waterflooding is defined as a forced imbibition process because water saturation increases due to viscous and capillary forces acting together. SI means water imbibes into the rock due only to capillary forces with no additional pressure applied. The main driving force in the SI process is capillary pressure, which is defined as the difference between the pressure of the non-wetting phase and the wetting phase. Viscous force is not sufficient for oil production in NFRs because of the low permeability of the matrix. In this review, the SI process is considered the main mechanism for oil recovery in NFRs.

There are two types of SI during matrix-fracture interaction: (1) co-current imbibition, for which the wetting phase and non-wetting phase flow are in the same direction as the face, and (2) countercurrent imbibition, for which the wetting phase and non-wetting phase flow are in the opposite direction from the same face [77,78], as shown in Figure 1.

2.2. Effect of Gravity on SI

The efficiency of the SI process in NFRs depends on several factors such as the petrophysical properties of the rock (porosity, permeability, heterogeneity, and wettability), IFT between the oil and water, initial water saturation, viscosity of the oil, temperature, mobility ratio, and matrix shape factor [80]. The authors of [81] used a 2D visual representation of core samples and SI tests for co/countercurrent imbibition to examine different parameters of the core and fluids, such as the orientation of the core, wettability, mobility ratio, IFT, and matrix shape. It was found that the vertical or horizontal orientation of the core can influence the fluid distribution in the porous media. In the case of a vertical position, the imbibed water was distributed as a more stable front, whereas a horizontal orientation resulted in a “single fingering” distribution in the case of SI between water and oil/kerosene. Figure 2 represents the schematic results of the countercurrent imbibition tests of oil-water and kerosene-water. Figure 3 shows the recovery factor results of different orientations and fluid types. Overall, kerosene-water has faster and higher oil production compared to oil-water SI because of the low viscosity of kerosene and the more favorable mobility ratio.

In terms of the rock orientation, vertical samples show higher oil recovery because of the uniform movement of water.

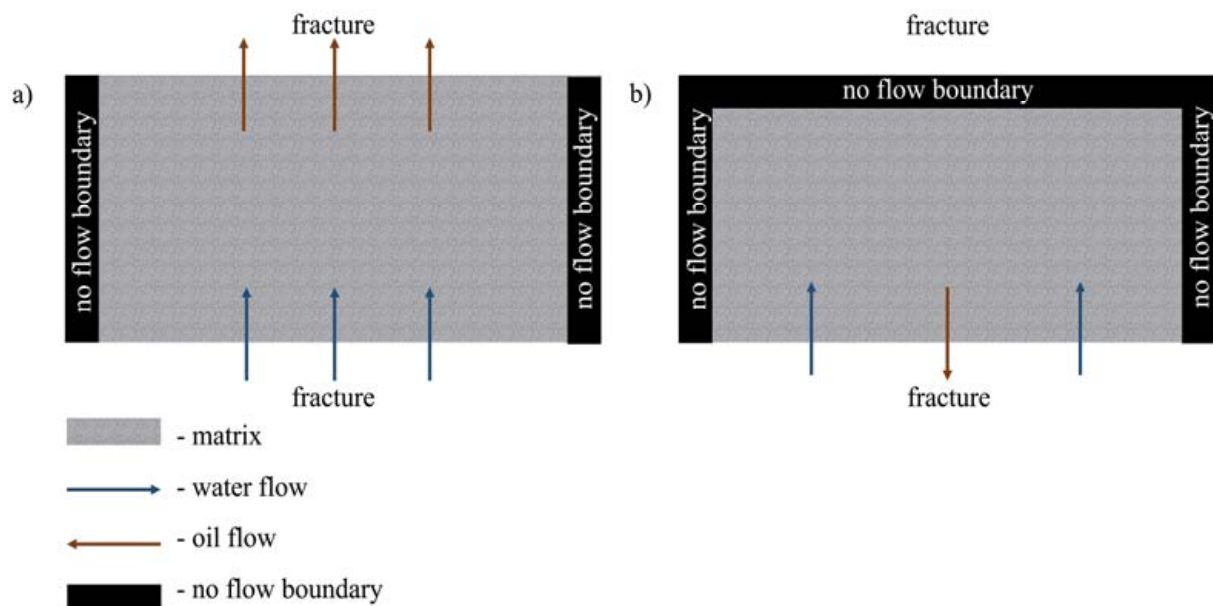


Figure 1. Schematic representation of (a) co-current flow and (b) countercurrent flow in NFR during SI [79].

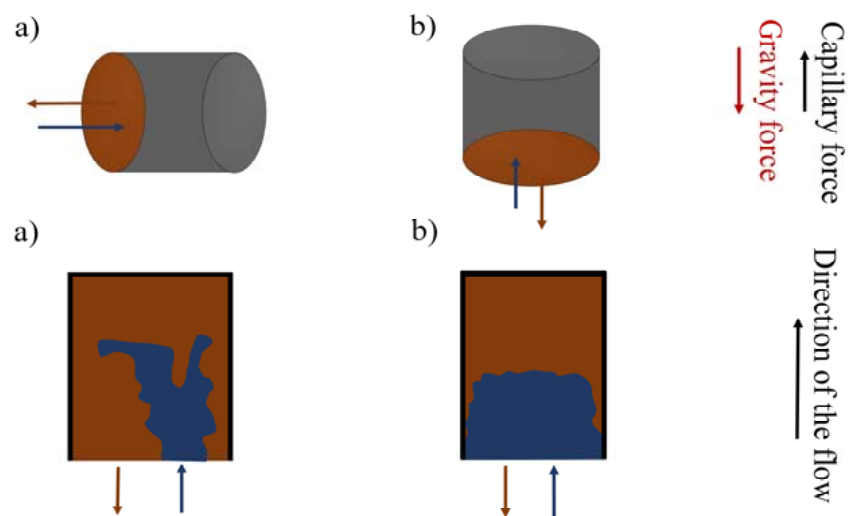


Figure 2. Schematic of the effect of sample orientation on fluid distribution. Countercurrent imbibition (a) in a horizontal orientation (without gravity effect) or (b) in a vertical orientation (with gravity effect) [81].

The effect of the core orientation on oil production can be described by the Bond number, which is defined as the ratio of gravity to capillary forces. The horizontal orientation excludes the effect of gravity, while in the vertical imbibition test, gravity affects oil production. The Bond number can evaluate the dominant forces in imbibition tests. If the matrix blocks have high vertical permeability and the density difference between oil and water is significant, gravity segregation may have a dominant effect on oil displacement.

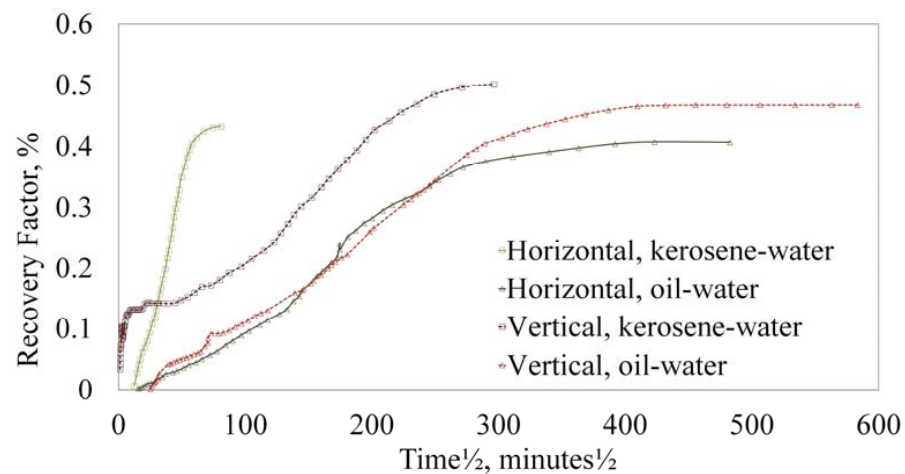


Figure 3. Recovery factor results of countercurrent imbibition tests for horizontal and vertical orientations of kerosene-water and oil-water [81].

Schechter et al. proposed their version of the Bond number, which is shown in Equation (1) [82].

$$N_B^{-1} = C \frac{\sigma \sqrt{\frac{\phi}{k}}}{\Delta \rho g H} \quad (1)$$

where

C	Constant, $C = 0.4$ for the capillary tube model
σ	Interfacial tension (N/m)
ϕ	Porosity (fraction)
k	Permeability (m^2)
$\Delta \rho$	Density difference between wetting and non-wetting phases (kg/m^3)
g	Gravitational acceleration (m/s^2)
H	Height of the medium (m)

The authors of [83] found that Equation (1) has some limitations. For example, it was established on a capillary bundle model, which cannot represent complex and tight rocks. In addition, although the capillary pressure is significant in tight rocks, other resistances cannot be neglected, such as surface forces. Therefore, the inverse Bond number needs to be further developed in the future [84].

The ratio of the capillary to gravitational forces and the conditions applied at the boundary conditions of the matrix can affect the flow direction during SI [85]. According to the authors of [86], capillary force dominates the imbibition process when the inverse Bond number is higher than 5, and gravity dominates the imbibition process when the inverse Bond number is lower than 1. In the intermediate range $1 < N_B^{-1} < 5$, both capillary and gravitational forces can be active in the displacement, and oil will be produced mainly from the upper part of the porous medium. If capillary forces dominate the spontaneous process, oil is produced in a countercurrent flow mode from all surfaces. The inverse Bond number is reduced by decreasing IFT or increasing the density difference, gravity become more important and, at the limit of very low inverse Bond number values, the flow is completely segregated by gravity. In this case, due to the flow segregation, the relative permeability of both phases is high and the flow is co-current. Hence, the orientation of the core in the SI test is an important parameter, and in a vertical orientation, both capillary and gravitational forces should be evaluated.

As was mentioned previously, gravitational force can affect oil production and also the directions fluids flow in. The Bond number is used to evaluate the significance of gravitational force, but Equation 1 is needed to improve that by including IFT and porous media. Experimental results can be affected by the core orientation. The experimental works

can only be used for simulation models where the core is one-directional and horizontal since even if gravity is neglected in simulation models, it still affects oil production. In addition, high gravity can lead to co-current imbibition. In this case, countercurrent flow cannot be evaluated correctly. Therefore, the experimental procedure should be established accurately to eliminate the effect of gravity for a completely capillary-driven process.

2.3. Effect of Matrix Wettability on SI

Matrix wettability is an important parameter in the SI process, which is driven by capillary forces in co/countercurrent flows [76]. Few research studies have been conducted to examine the effect of the wettability of NFRs during imbibition tests. The SI process of conventional water flooding cannot occur in an oil-wet system because of the positive capillary pressure [87,88]. The authors of [89] provided experimental research in which water-wet sandstone and oil-wet carbonates were used for co/countercurrent imbibition. The oil-wet carbonate core showed the lowest recovery factor, and the application of polymer and surfactant increased the incremental oil recovery by up to 6–8% (Figure 4). Hot-water capillary imbibition showed the highest oil recovery for all experiments, but the application of hot water could increase the operational cost significantly compared to chemical injections. Imbibition experiments in water-wet sandstone showed better performance than carbonate rock in all cases; even the production of heavy oil (650 cp) in water-wet sandstone was higher than light oil recovery in oil-wet carbonate cores.

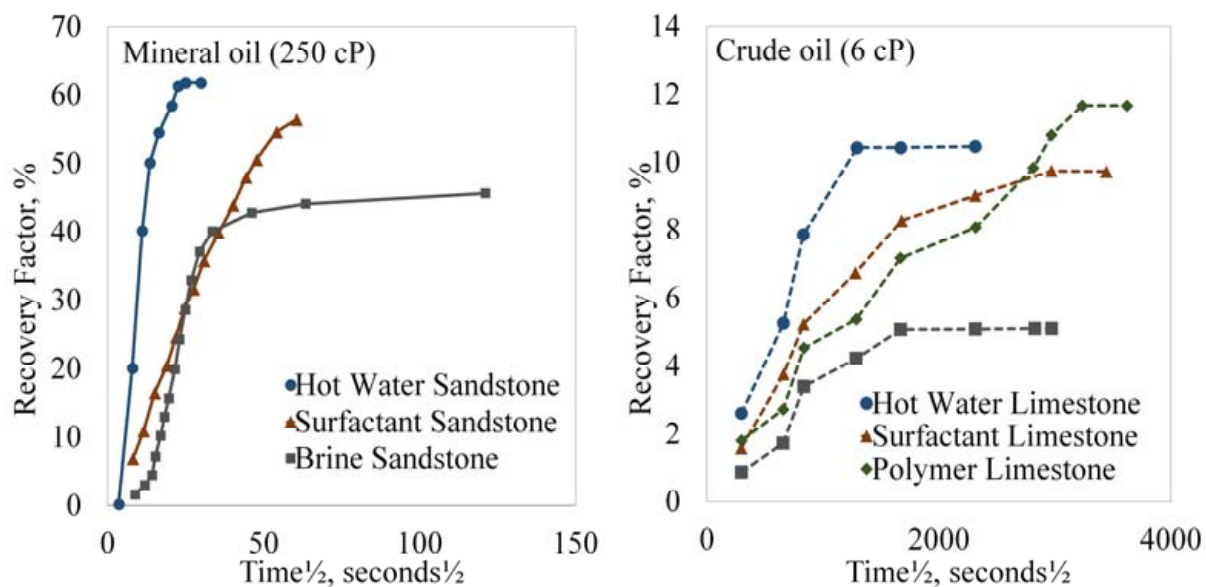


Figure 4. SI results for different imbibition fluids in water-wet sandstone and oil-wet limestone core samples [90].

Water imbibition was studied in unconsolidated sand packs that were prepared to duplicate the matrix and put in a meshed holder to create a fracture-matrix interaction [80]. Experiments were conducted for different wettability states to examine the effect of wettability on water imbibition in the fractured reservoir. In the process of the waterflooding experiment, oil was firstly displaced from fractures that had high permeability, and only after that was water imbibed spontaneously from fracture to matrix due to capillary and gravitational forces. The SI process occurred through countercurrent flow. Figure 5 shows the oil recovery of water imbibition experiments for different wettability conditions. It can be noted that wettability significantly affects the imbibition performance, and the total recovery is up to 30% higher for a 100% water-wet system compared to a strongly oil-wet state. In addition, the oil recovery rate is the fastest in highly water-wet conditions.

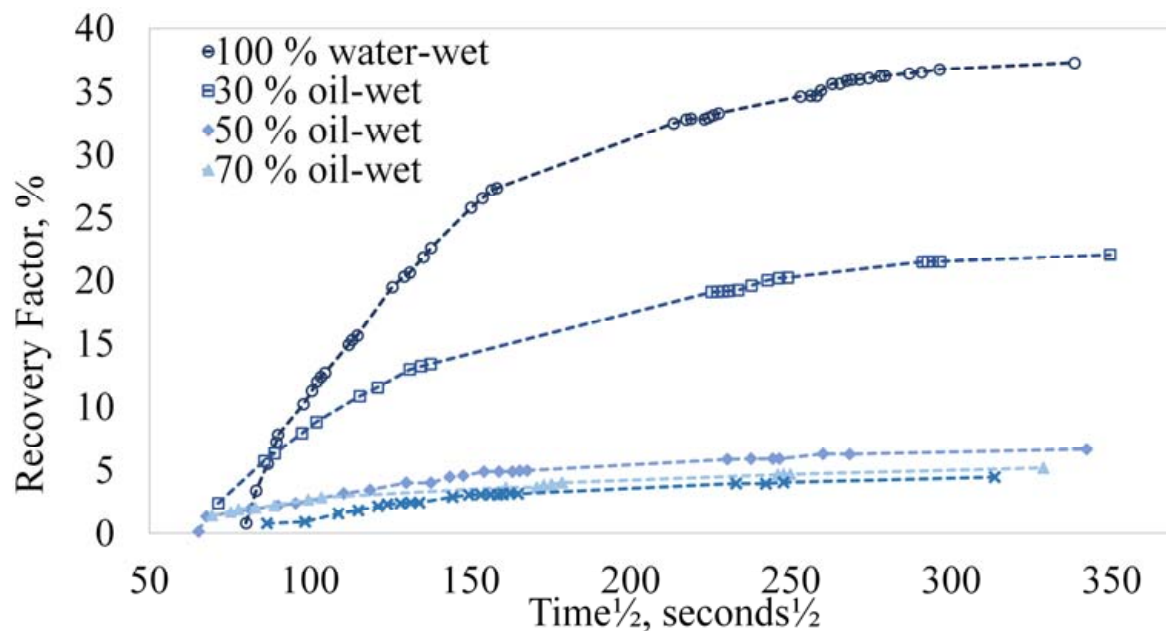


Figure 5. Water imbibition experiment in artificial fractured core with different wettability states [80].

The authors of [80,89] showed that wettability can significantly influence the performance of the SI process. In [89], they used chemicals such as polymers and surfactants to improve the mobility ratio and decrease IFT correspondingly. However, the more efficient method is to change wettability to a more water-wet state so that capillary force is used as the driving force in the SI process. In addition, the application of chemicals or hot water can result in high operational costs.

A non-water wet state leads to low oil production because of insufficient capillary force. To overcome this problem, wettability alteration is an effective mechanism to increase oil production in fractured reservoirs. Several EOR methods are used to change wettability to more water-wet conditions, such as LSW flooding, nanofluids, and surfactant injection [55,91]. LSW injection is considered a cost-effective and ecologically safe EOR method as it does not require special chemicals and can be prepared by diluting water or adding a specific ion concentration. LSW can imbibe spontaneously from fracture to matrix and alter the wettability to more water-wet conditions. NFRs at the core scale can be investigated in several ways and using different approaches, as is shown in further sections. These methods can also be used to evaluate the performance of LSW in the SI process. Table 2 shows the effect of different parameters on the performance of SI in NFRs. As the SI process is divided into co- and countercurrent flows, they are described separately. In this review, wettability is analyzed deeply as it directly affects the capillary force. In addition, the gravitational force is taken into account because it is also one of the driving forces during the SI process, though other parameters such as rock properties, oil, and brine properties affect SI and co/countercurrent flows. The authors of [92] studied the effect of different parameters on the SI process using machine learning (ML). Viscosities of displaced and displacing fluids, IFT, porosity, permeability, length of the core, and imbibition time were analyzed to identify the most significant parameter. It was found that imbibition time had the greatest effect on recovery during SI; after that, IFT and length then greatly affected SI. In addition, it was concluded that the ML technique can be used to predict recovery performance during SI. Still, ML is dependent on input parameters that are measured experimentally, and the accuracy of experiments is crucial for further studies.

Table 2. Effect of different parameters on SI in NFRs.

Effect	Co-Current Imbibition	Countercurrent Imbibition	General SI
Gravity	Increases	Decreases	Co-current flow dominates
IFT reduction	Increases	Decreases	Capillary force decreases and fluids move under gravity
Wettability	Decreases	Decreases	Oil-wetness decreases the oil recovery
	Difference between co- and countercurrent becomes negligible as wettability becomes more oil-wet		
Initial water saturation	Water is easily imbibed into pores		
Matrix porosity	Water is easily imbibed into pores		
Permeability	Water is imbibed more easily as matrix permeability rises		
Viscosity	High oil viscosity creates resistance to flow		
Mobility ratio	A lower mobility ratio increases the SI process		
Temperature	Increases the imbibition rate		
Length of the core	Co-current flow dominates over countercurrent flow as the length of the core increases	Decreases as the length decreases	

3. Experimental Investigations of Co/Countercurrent Imbibition

Experiments of SI in porous media are the main method to measure oil production by SI and predict the rate of oil recovery from fractured reservoirs. In the past decades, numerous experimental methods and setups were introduced, as well as advanced techniques to investigate various factors that affect SI. Table 3 represents the experimental methods used to investigate the SI process in NFRs and the main advantages and limitations of each method.

Table 3. Comparison of different methods to measure SI in NFRs.

Experimental Methods to Evaluate SI in NFRs	Parameters Measured	Accuracy in SI Evaluation	Advantages of the Method	Disadvantages of the Method
Weighting method Amott cell	Oil production during SI	Medium	Easy to operate, cost-friendly	Time-consuming, does not separate co/countercurrent imbibition, only vertical orientation of the core, gives non-unique solutions of simulation models during validation, scaling is sensitive, oil bubbles can be formed on the surface of rock and affect the accuracy of the results.
Amott cell with boundary condition (OOE, TEO, OOCO)	Oil production during co/countercurrent SI	Medium	Separate co/countercurrent SI, cost-friendly	Time-consuming, TEO does not separate co/countercurrent flows, OOCO requires a specific experimental setup that can collect oil production during co/countercurrent imbibition.
CT scan test	Water saturation profile during SI	Strong	Fast, shows porous media and fluid distribution, can be set up together with a core holder, co/countercurrent flow can easily be distinguished.	Resolution of CT scan is crucial, CT numbers of crude oil and brine should be known, CT scan pictures can have noises affecting the accuracy of the test, CT number represents the density contrast (as the density contrast can be low, the CT scan pictures do not show the contrast in the picture), requires a special dopant to increase the contrast, can be difficult to interpret, expensive.
NTI	Water saturation profile during SI	Strong	Fast, shows macroscale images of the core and fluid distribution, co/countercurrent flow can easily be distinguished.	Expensive, can be difficult to interpret, camera resolution is important, requires radioactive tracer in samples, radioactivity.
MRI/NMR	Water saturation profile during SI	Strong	Fast, shows pore structure, pore geometry, and fluid distribution, co/countercurrent flow can easily be distinguished.	Expensive, requires a special dopant to increase the contrast, can be difficult to interpret, camera resolution is important, signal can be affected by the magnetic properties of the surroundings, can be harmful to humans if not applied properly.

3.1. Weighing Method

The weighing method is commonly used to measure SI [3,81,93]. a schematic illustration of this method is shown in Figure 6. After the core sample is immersed in the imbibing fluid, the weight change of the core sample over the imbibition time is monitored and automatically recorded by a high-precision electronic balance. Oil production by SI can be calculated according to the density difference between the imbibing fluid and oil [94,95].

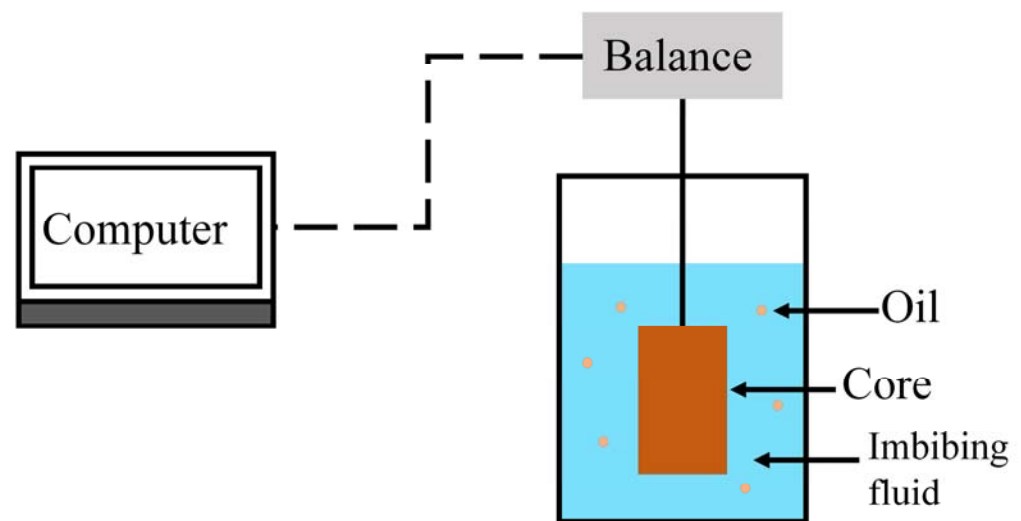


Figure 6. Schematic illustration of SI experiment using the weighing method.

3.2. Amott Cell Method

One of the simplest, easiest, and most widely used experimental setups to conduct SI tests is imbibition cells or Amott cells. The oil-saturated core sample is put into the imbibition cell, which is filled with displacing fluids that spontaneously imbibe into the core and displace the saturating fluid. The volume of displaced fluid can be calculated by a scale located at the bottom or the top of the Amott cell, depending on the type of displacing fluid [96]. It should be noted that for SI experiments, the immersed core plug in the imbibing fluid represents the matrix medium surrounded by fractures filled with injection fluid.

3.3. SI Test with Different Boundary Conditions

The Amott cell and weighing methods give information about SI when all the faces of the core are open. The core is placed vertically most of the time. The measured results do not distinguish the co/countercurrent flows, and it is difficult to analyze each flow separately. Therefore, different designs are used to separately measure co/countercurrent imbibition by changing the boundary conditions as follows:

- (1) *All Faces Open (AFO)*—In this arrangement, co- and countercurrent flows are not distinguished, as shown in Figure 7a. AFO is commonly used as a SI test, but it is difficult to differentiate the co- and countercurrent flows, which need to be separated to perform numerical simulations [3,91].
- (2) *One Open End (OOE)*—the core is coated around all faces except one (Figure 7b). This condition can create countercurrent linear flow [91,97]. In this condition, the flow is driven by capillary pressure, which includes water invasion, oil expelling, and capillary back pressures [3].
- (3) *Two Ends Open (TEO)*—this condition creates linear co- and countercurrent flows (Figure 7c). However, the two flows are occurring at the same time and cannot be separated [3,88,91].
- (4) *One Open End and One Isolated End (OOCO)*—one open end creates a countercurrent flow, and the isolation of the other end can catch the oil production from the co-current flow (Figure 7d). This technique allows the co- and countercurrent flows to be measured separately [98,99].

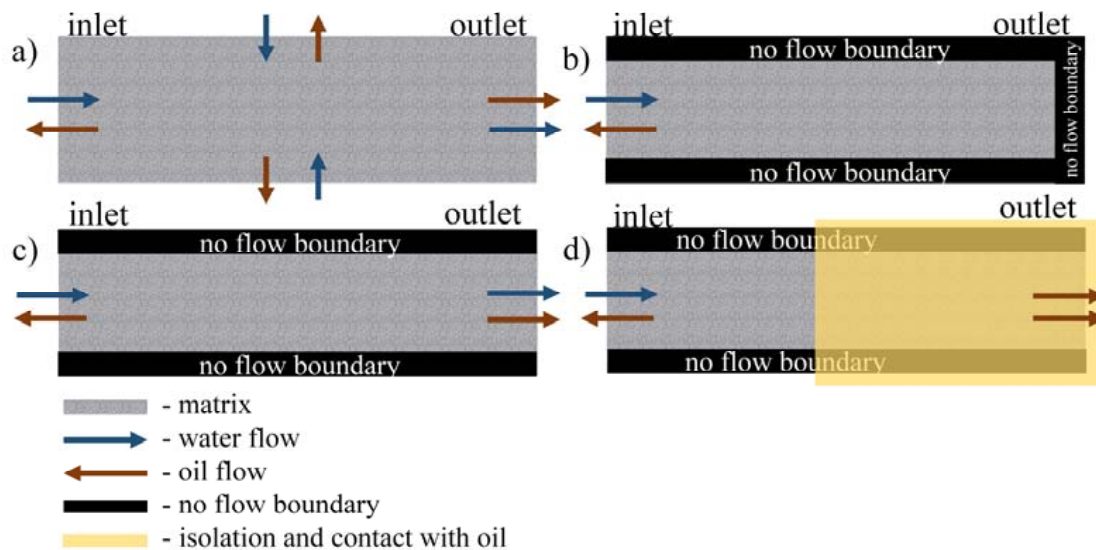


Figure 7. Schematic diagram of boundary conditions for core samples. (a) All Faces Open (AFO); (b) One Open End (OOE); (c) Two Ends Open (TEO); (d) One Open End and One Isolated End (OOCO) [100].

The Amott cell and weighing methods measure the oil production during the SI process. However, the application of specific boundary conditions makes the experiments complicated. In addition, the Amott cell and weighing methods are sensitive and time-consuming. The orientation, size of the core, and properties of the rock and fluids affect the experimental measurements. Oil production measurements alone cannot give a comprehensive analysis of NFRs' performance. In this case, the fluid distribution is more important than the oil recovery measurements because it can give more detailed information and can be applied for the validation of numerical simulations.

3.4. CT Scanning Method

The CT scan test is a powerful tool that is used in petroleum engineering. It can also be used to analyze the SI process and measure the in situ water saturation distribution. The measurements from CT scan tests can be applied to validate numerical studies of co/countercurrent flows. The authors of [101] provided detailed information on the application of CT scans in measuring porosity, permeability, and fluid distribution. They gave 2D and 3D images of the core with different CT numbers.

The fluid movement during the SI process in NFRs can be investigated by observing the in situ water saturation distribution. Dynamic alteration of water saturation in porous media during SI provides important data on the co/countercurrent fluid flows. Figure 8 presents the common CT scanner test that measures the water saturation profile. Generally, water saturation is shown as a function of distance and the square root of time, which is defined as the Boltzmann variable ω [102].

3.5. NTI, MRI, and NMR Methods

The in situ water saturation distribution can also be measured using magnetic resonance imaging (MRI) during SI tests [105]. The authors of [105] investigated the effect of the initial water saturation on the fluid distribution during the SI process. Furthermore, the authors of [106] provided comprehensive research on co/countercurrent imbibition tests and measured the water saturation distribution inside the core during the SI process. MRI makes it possible to visualize the fluid movement inside the core and understand the behavior of co/countercurrent flows. In addition to the MRI, which provides pictures of the pores of the core, nuclear tracer imaging (NTI) can be used to produce macroscale images of the core and matrix–fracture interaction [107].

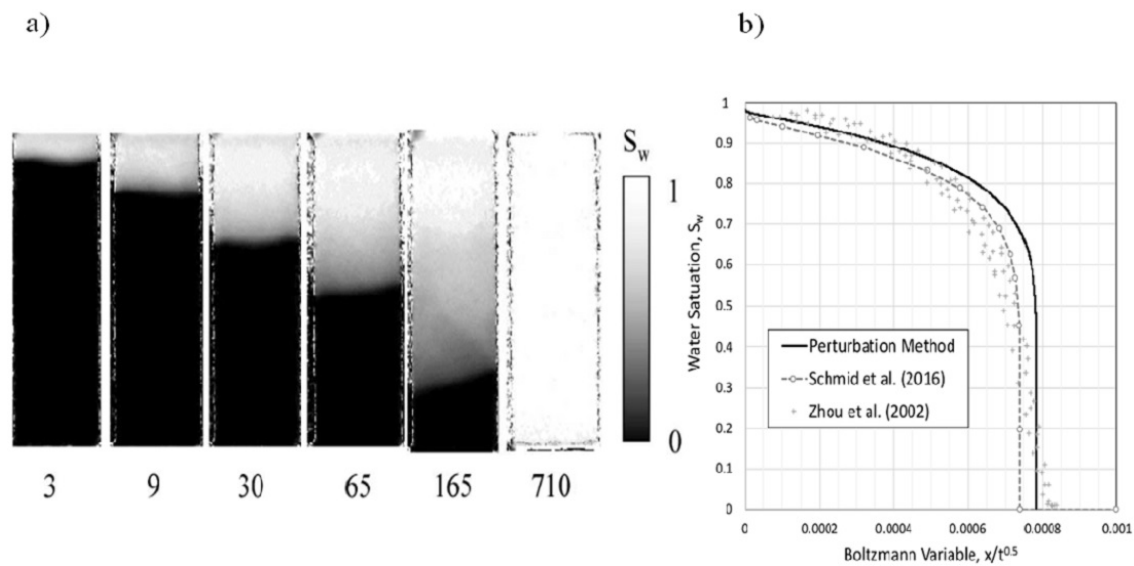


Figure 8. CT scanner test results. (a) 2D images of the core during the SI test in diatomite. Time in minutes [103]. (b) Water saturation profile as a function of distance and the square root of time [104].

Nuclear magnetic resonance (NMR) technology is an advanced method for analyzing and detecting the characteristics of porous media. It provides valuable information on various features such as porosity [108,109], pore size distribution [110], permeability [111], oil–water saturation [112], wettability [113], and isotropy degree [114]. Over the years, NMR has been utilized in numerous experimental studies, including the identification of cracks, the evaluation of pore distribution, and the characterization of internal rock structures. Recently, NMR has also been employed to investigate the mechanisms of SI [115].

The authors of [115] investigated the characteristics of oil and water distributions in tight oil reservoirs at the pore level during the SI process. They employed NMR testing and imbibition experiments to obtain their results. First, they utilized a combination of NMR and mercury injection capillary pressure (MICP) to examine the distribution of oil and water in the SI process. Next, they utilized MRI and pseudo-color mapping to visualize the distribution and evolution of oil and water during the SI process. Finally, they proposed a new concept called the “spontaneous imbibition pathway” to define the cause of the SI rate. Their findings revealed the pore characteristics and the distribution of oil and water during the SI process, which is important for the efficient development of tight oil reservoirs.

As fluids in fractured reservoirs move co/countercurrently depending on various factors (that were presented previously), an accurate experimental procedure should be established. If it is important to separate two flows, boundary conditions should be applied correctly. If capillary force is set to be the main driving mechanism, the Bond number and the gravitational force should be evaluated or the core orientation can be established as horizontal. The in situ water saturation distribution can give more detailed information about fracture–matrix interaction and the results can be used in simulation models. Pictures of porous media and fluid distribution give more specific information than SI tests alone, but the methods are costly and more advanced compared to simple Amott cell or weighing methods.

4. Experimental Studies of LSW in NRFs

EOR in fractured reservoirs with a neutral to a preferential oil-wet low-permeability matrix is a big challenge in the oil industry since the application of secondary water flooding is not a suitable oil recovery method in NRFs [116–118]. Adding chemicals such as surfactants can improve the oil recovery, decrease IFT, and alter the wettability toward more water-wet conditions [42,119]. Given the economic issues including the high cost

of applying chemical additives at the field scale, it is important to investigate cheap and efficient methods such as LSW or EW injection to alter wettability toward water-wet states. To investigate the wettability alteration effect, many experimental works have been conducted in sandstones and carbonates [120–124]. This section highlights some of the related SI experimental results.

SI tests represent the behavior of a single matrix-fracture system. Since NFRs are mostly carbonates, the main emphasis of this study is on that mineralogy. Table A1 collates about 20 research works that studied the SI process using LSW and smart water. These studies include investigations of the effect of the salinity and composition of the imbibing water and its effective parameters on its performance in carbonate formations. In addition to proving the effectiveness of LSW or EW in carbonates, several researchers investigated other important parameters, such as the temperature, connate water saturation, core permeability, and core length, which affect this EOR method [88,98,124–128].

As can be seen, even though several factors such as the rock and fluid properties were different in these studies, in all cases, an improvement in oil production was observed for diluted seawater or seawater spiked with PDIs (Ca^{2+} , Mg^{2+} , and SO_4^{2-}) in NFRs.

In the literature, few experimental studies have investigated LSW performance in NFRs, but more research has been conducted in tight sandstones, which has similar matrix-fracture interactions. In addition to the application of SI in naturally fractured carbonate reservoirs to represent the matrix-fracture system, SI has been put forward as one of the fundamental mechanisms to understand the complicated liquid–formation interaction during hydraulic fracturing operations in a tight sandstone formation. As a tight sandstone reservoir has low permeability and connectivity, hydraulic fracturing is commonly used in the production process [129–132]. During this process, water imbibes into the matrix blocks spontaneously and displaces hydrocarbon from the matrix [133].

The authors of [134] studied the influence of salinity and mineral components on imbibition capacity by a weight-increasing method in tight sandstones with different amounts of minerals. Their experimental results showed that the content of wetting clay minerals (illite/smectite mixed layer, illite) has a positive influence on the imbibition capacity due to the forming of a diffuse electric double layer or constitution water on clay layers as a result of liquid contact with the wetting clays [135,136]. Thus, the expansion of micro clay layers leads to more liquid absorption. However, salinity can restrain the thickness of the diffuse electric double layer and restrain the expansion of the clay layer. Therefore, salinity has a negative impact on the SI process and can decrease the maximum volume of an imbibed liquid. The effect of LSW on oil recovery in tight Berea sandstones was investigated [137]. The researchers conducted SI experiments at 80 °C with salinity ranging from 0.021% to 2.1% TDS. Their results demonstrated that the optimal salinity for LSW EOR was 0.21% TDS brine for their conditions, which enabled them to produce the highest oil recovery of 4.5% OOIP. They also modified the capillary pressure and relative permeability curves through history-matching, then applied them to the field scale model constructed by micro-seismic data. Studies were conducted for sandstone formations with different mineralogies and correspondingly different mechanisms of LSW imbibition. However, experimental and numerical approaches can be used for investigations of naturally fractured carbonate rocks.

Most research works show the importance of LSW application in carbonates. There are lots of parameters and factors affecting the performance of LSW imbibition and no specific screening criteria for LSW that can be applied universally. NFRs add difficulties in LSW application because of their heterogeneous formation and fracture–matrix interaction.

Generally, high temperature, high permeability, and the presence of connate water saturation have a positive effect on the imbibing process and oil production. Most experimental works are conducted for the vertical position and all face open boundary conditions, which represent the multidimensional SI process. There are a few experimental works for standalone co- or countercurrent imbibition using LSW that indicate that the core length is an important parameter that controls the countercurrent flow. In general, the countercurrent flow is reduced by shorter core lengths, and for core lengths below a critical value,

the countercurrent oil flow can be eliminated. To extend our knowledge, it is crucial to conduct a comprehensive experimental study of LSW imbibition using specific boundary conditions to replicate the co/countercurrent flows that occur in NFRs. Furthermore, these experimental data can be used for simulation studies to calculate other parameters that are needed for the evaluation of NFRs' performance and LSW injection in NFRs.

5. Simulation Studies of LSW in NFRs

Simulation studies can give additional information about the processes that occur during oil production in NFRs. For example, simulation of the SI process in fracture-matrix interaction can reveal the water saturation distribution during capillary-driven movement of fluids and enable researchers to calculate the relative permeability and capillary pressure curves. In addition, simulations enable researchers to analyze the performance and differentiate between co- and countercurrent flows in the SI process. SI involves gravitational, viscous, and capillary forces, but in most cases, the capillary effect is neglected, which can lead to uncertainties in the recovery performance. The capillary force is an important parameter in the SI process and is considered the main driving force. Investigation of capillary forces can be carried out by distinguishing between co- and countercurrent flows. Several simulation studies have been conducted to study LSW injection in sandstone and carbonates. However, there is no good simulation study that can show the performance of LSW during the SI process in fractured formations. In this section, the general methods of LSW modeling are presented, which can be used later to model the LSW imbibition process in fracture-matrix interactions by applying dynamic wettability alteration.

Modeling of LSW at the core scale investigates various proposed mechanisms that were mentioned previously in the paper. It is believed that the wettability alteration is the dominant mechanism that leads to the increase in incremental oil recovery [9,138]. Therefore, the main idea of modeling LSW is to show the wettability alteration to more water-wet conditions. Wettability alteration can be represented by changing the relative permeability curves [139,140]. As a result, interpolation is introduced, which calculates relative permeability values between two opposite conditions. The relative permeability values of high-salinity water (HSW)/oil and LSW/oil are calculated experimentally and considered as input parameters of simulations. In most cases, the relative permeability curves are drawn by matching the oil recovery results during core flooding experiments. There are different simulation software available to model LSW imbibition such as Eclipse, GEM of CMG, PHREEQC, UTCHEM, and so on. Modeling LSW can be categorized into black oil modeling (the simplest), compositional modeling, and 1D numerical modeling [139].

During the interaction of LSW/oil/rock, the ionic composition of the water in the porous media is changed and a new relative permeability value is formed, which is estimated by an interpolation approach between the HSW/oil and LSW/oil measured relative permeability. The interpolation coefficient may vary according to the dominant wettability alteration mechanisms, such as calcite dissolution, MIE, and EDL expansion [141]. Wettability alteration is modeled using the shift of the relative permeability and capillary pressure curves, as is described by Equations (2) and (3) [142]:

$$k_{rw}^{altered} = (1 - \tau_{kr})k_{rw}^{HSW} + \tau_{kr}k_{rw}^{LSW} \quad (2)$$

$$k_{ro}^{altered} = (1 - \tau_{kr})k_{ro}^{HSW} + \tau_{kr}k_{ro}^{LSW}$$

$$p_c^{altered} = (1 - \tau_{pc})p_c^{HSW} + \tau_{pc}p_c^{LSW} \quad (3)$$

Interpolation between the initial and final conditions can be achieved in the relative permeability, capillary pressure curves, and contact angles [143]. Based on the active mechanism, corresponding parameters can be introduced as interpolation coefficients. For example, the composition of PDIs or carboxyl groups of oil is used to model multicomponent ionic exchange mechanisms. In addition, the calcite volume fraction is also utilized to simulate rock dissolution [142]. The interpolation coefficient can be a function of water

salinity, the concentration of potential determining ions, the mineral fraction, total ionic strength, the concentration of the carboxyl group, and so on [144].

One of the simplest models of LSW was introduced by the authors of [145]. In this model, the relative permeability values are dependent on the salinity of the injected brine. The model does not consider the ionic composition of water, which is a crucial parameter in LSW injection. Potential determining ions play an important role in wettability alteration. Therefore, the model does not fully describe the behavior of LSW. In another work, the authors of [146] investigated two approaches to modeling LSW in sandstone. The first shows a linear relationship between the residual oil saturation and the salinity of the injected brine, as modeled by the authors of [145]. The second model considers a multicomponent ionic exchange mechanism. It was concluded that different mechanisms affect crude oil, brine, and rock interactions such as MIE, pH increase, and wettability alteration. Hence, a linear relationship model cannot combine all these effects. In addition, the authors of [146] did not consider the interaction between clay and brine, which is important in LSW and is defined as one of the main mechanisms. However, they presented the effect of the capillary pressure curve in LSW and concluded that capillary pressure in the modeling of LSW cannot be ignored. The same conclusion was proposed by the authors of [147], who showed that the capillary pressure curve affects the history matching of the pressure drop profile. They used the GEM module of CMG to simulate ion exchange and aqueous and mineral reactions.

The authors of [148] compared gradual with instantaneous wettability alteration through simulation models using PHREEQC. They proposed that wettability is a time-dependent function. The interpolation coefficient used for relative permeability curve calculation was defined as a function of the time and ion concentration. The results showed that gradual wettability alteration can occur at the beginning of LSW injection. As temperature decreases, the difference between gradual and instantaneous wettability alteration is negligible.

Lately, the machine learning (ML) technique has been gaining attention in the evaluation of recovery performance through the application of LSW. Data-driven modeling is used to predict the recovery performance and conduct sensitivity analysis of LSW flooding. In one article, an artificial neural network (ANN) model was used to simplify the process of evaluating LSW flooding [149]. The empirical model consists of several parameters such as the dilution of HSW, mobility ratio, oil and rock properties, and production data. The authors used the ANN model to calculate the recovery factor after LSW flooding, and this study can be applied as a preliminary stage of the evaluation of LSW performance. Another example of the application of the machine learning technique in LSW evaluation is [150]. The authors compiled experimental studies of LSW flooding in carbonates and analyzed the important parameters that affect the LSW flooding efficiency. Different ML models were applied, such as ANN, support vector machine (SVM), and decision tree (DT). Going beyond the research work [149], the authors also included the PDI concentration, acid and base numbers of the oil, and temperature. However, despite extensive analysis of the different parameters that affect LSW flooding in carbonates, it is still difficult to find the exact parameter and mechanism that lead to increased wettability alteration during LSW injection. The authors of [151] conducted a Random Forest regression to evaluate the different parameters that influence LSW flooding in carbonates. Based on a single carbonate reservoir example, they modeled 1000 field designs with different temperatures, LSW and HSW compositions, and volumes of water injected. They concluded that the composition of sulfate ions and the volume of LSW injected are the most important parameters that affect LSW performance. However, the data provided were gathered from simulation models in which wettability alteration was shown through shifting the relative permeability curves.

There are several studies on the application of machine learning techniques for LSW flooding in sandstone and carbonates. However, no recent studies have been found for NFRs or tight reservoirs. In addition, most research works have been carried out using simulation data, leaving a lack of experimental work, which means certain uncertainties

persist and there is a reliance on assumptions. In addition, many parameters need to be investigated because the exact mechanism of LSW is still under research. There are no general screening criteria for the application of LSW in carbonates and sandstone. Despite this, the application of the ML technique is a promising tool in the prediction of LSW performance. In addition, according to [152], the ML technique has potential to be applied to solve the differential equations used in reservoir simulation and modeling of NFRs.

Modeling of LSW imbibition in NFRs is not well investigated and there are few research works reported in the literature. A single-porosity model and a dual-porosity model were created to investigate the fracture-matrix interactions [153]. A dual-porosity model is widely used in the simulation of fractured formations. However, a dual-porosity model leads to overestimation of the recovery performance. The same approach was also used to model LSW flooding in NFRs. The authors of [154] conducted a simulation study where they prepared a matrix block model and a field scale model of the Qamchuqa Reservoir. A fine-scale model was prepared to investigate the matrix-fracture interactions and fluid flow due to capillary and gravitational forces with a dual-porosity approach. Relative permeability curves were calculated through core flooding experiments. The change in the capillary pressure curve was neglected, which led to limitations of the work as it ignored imbibition. However, the presented workflow for calculating the relative permeability curves and modeling the reservoir sector can also be applied to the calculation of capillary pressure curves. It was stated that wettability alteration was revealed by changing the saturation exponents of the relative permeability curves. In the fine-scale model, the contribution of capillary force was significant, as can be seen in Figure 9.

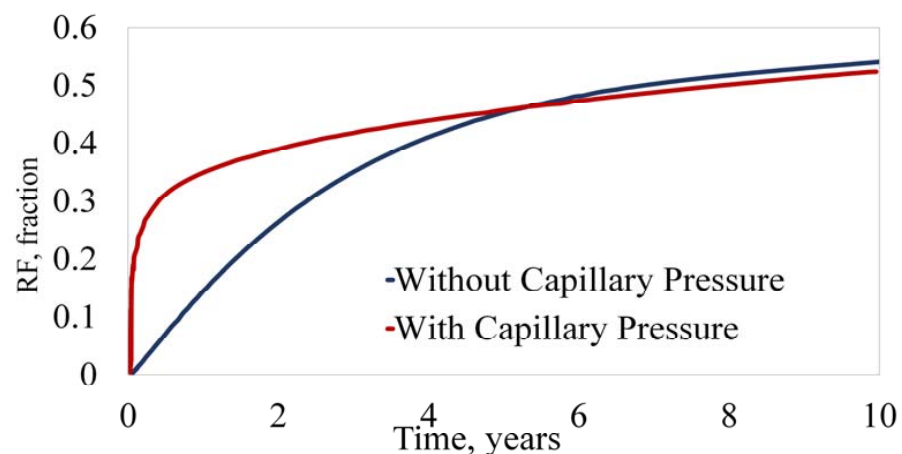


Figure 9. Recovery factor results for the fine-scale model with and without the capillary pressure effect [154].

A fine-scale model was provided to investigate the SI process between the matrix and fracture in NFRs, and the results of the fine-scale model were compared using upscaling with a dual-porosity model [155]. LSW injection was modeled using the simple salt concentration. Simulations fixed the relative permeability curves, which were not changed during LSW injection, and the researchers only changed the capillary pressure curve to fully model the capillary-driven flow between matrix and fracture.

The authors of [99] provided a simulation work in which wettability alteration during co-current imbibition was modeled. A mixed-wet 1D core was considered a matrix with two sides open at the inlet and outlet. The model was constructed such that water and oil moved in countercurrent flow from the inlet, and oil moved co-currently from the outlet. Wettability alteration was modeled using the adsorption component. The level of wettability alteration was calculated using the interpolation coefficient, which was dependent on the adsorption component concentration. The interpolation coefficient was used to define the relative permeability and capillary pressure curves. Using simulation, the researchers analyzed several parameters that affect co/countercurrent imbibition, such as the mobility

ratio, capillary back pressure, wettability, and initialization time of wettability alteration. It was found that wettability alteration mostly occurred near the inlet and affected the countercurrent imbibition more than the co-current. The effect of the wettability alteration component on co-current imbibition could be seen in the late period. As a result, the recovery performance of countercurrent imbibition was higher than the co-current one. The model was constructed for immiscible and incompressible fluids in which the wettability alteration component was dissolved in the water phase. The wettability alteration component directly affected the relative permeability and capillary pressure curves. This approach simplifies the wettability change by ignoring the geochemical reactions between the crude oil, brine, and rock. In addition, the application of the adsorption component describes the wettability alteration of the surfactant injection rather than LSW imbibition.

Numerical studies of LSW imbibition in NFRs offer an interesting approach as LSW changes wettability to more favorable conditions and increases the imbibition of water into the matrix system. Currently, there are lots of analytical studies of co/countercurrent flow in NFRs, while there are only a few examples of modeling LSW in NFRs. The reason for this situation is the complexity and novelty of LSW. Modeling LSW involves compositional modeling of oil and water, geochemical reactions, and dynamic wettability change through shifting relative permeability and capillary pressure curves. Analytical equations of the SI process involve several assumptions, such as the incompressibility of fluids and the homogeneity of rock. This is based on the simple Darcy's law and the mass conservation equation. Further modeling of the SI process should include crude oil, the rock surface, brine interactions through geochemistry, and dynamic wettability alteration.

6. Numerical Modeling of Co/Countercurrent Flows

Numerical studies of co/countercurrent flows have been conducted to simulate the flow of water and oil in the fracture-matrix interaction. Analysis of the fluid transfer in NFRs is a complex and difficult process because the fracture and matrix have different porosity and permeability. A common single porosity model cannot accurately estimate the co/countercurrent flow of NFRs. Co-current and countercurrent flow show different characteristics. For example, co-current imbibition leads to faster and more oil recovery than countercurrent imbibition [78]. Numerical studies can also give more information about the fluid transfer in NFRs, such as calculating the relative permeability and capillary pressure curves. This can reduce the number of experiments that take a long time. Finally, a combination of numerical and experimental studies can give a comprehensive evaluation of NFRs' performance.

The analytical equation to model the spontaneous imbibition process in NFRs combines the mass conservation equation and Darcy's law. The analytical equation for SI is derived from the one-dimensional flow of two immiscible, incompressible phases in porous media [78,100,102,156–162]. The following assumptions are considered to derive the analytical equation:

- Fluid flow is one-directional for co-current imbibition.
- Rock properties are homogeneous and isotropic.
- Phases are incompressible and immiscible.
- System is isothermal.
- Gravity effect is neglected.
- Inlet capillary pressure equals zero.
- No capillary back pressure.

The co-current spontaneous imbibition flow is shown in Equation (4) through the nonlinear diffusivity equation.

$$\frac{\partial}{\partial x} \left(D(S_w) \frac{\partial s}{\partial x} - f(S_w) q_t \right) = \frac{\partial S_w}{\partial t} \quad (4)$$

The countercurrent spontaneous imbibition flow is shown in Equation (5).

$$\frac{\partial}{\partial x} \left(D(S_w) \frac{\partial S_w}{\partial x} \right) = \frac{\partial S_w}{\partial t} \quad (5)$$

where the diffusivity coefficient $D(S_w)$ is a function of capillary pressure, saturation, and relative permeability, as shown in Equation (6).

$$D(S_w) = -\frac{k\lambda_{nw}\lambda_w}{\lambda_t} \left(\frac{\partial P_c}{\partial S_w} \right) \quad (6)$$

The authors of [78] provided numerical studies of co- and countercurrent imbibition flows assuming zero capillary pressure at the inlet. The simulation models were validated using analytical solutions. Based on their simulation studies, they concluded that co-current imbibition is more efficient and results in more oil production than countercurrent imbibition. In addition, they found that co-current flow is dominant in the matrix, which is in partial contact with water. Sensitivity analysis was also conducted to assess the oil and water relative permeability exponents, initial water saturation, viscosity ratio, and length of the core.

Saturation can be measured at small time intervals during SI [163]. The researchers validated the model with in situ water saturation measurements using CT scanning. They presented the derivation of general analytical equations for co-current and countercurrent flows and solved the equations using the backward difference method. Water saturation versus ω , which is a function of distance and time, was compared with the experimental data. This technique helps to simplify the measurements of relative permeability curves, which can be a long and difficult process, especially for fractured carbonates and tight sandstones.

The authors of [102] conducted a numerical analysis of co- and countercurrent flows using fractional-flow theory. The simulation results were validated using experimental measurements of the in situ water saturation distribution in limestone and diatomite and were valid for the early imbibition. The analytical solutions were given for three main wettability states: strongly water-wet, weakly water-wet, and mixed-wet. The researchers also concluded that co-current flow gives faster oil recovery, and the waterfront is more piston-like, compared to countercurrent flow. However, the difference between co-current and countercurrent flows became negligible as the wettability changed to mixed-wet. In addition, they estimated a big difference in the oil recovery and imbibition time between strongly water-wet and mixed-wet systems.

Experimental studies were conducted to measure water saturation using CT scanning [156]. In addition, numerical studies were conducted [102] to solve the analytical equations of SI and compared the solutions with experimental measurements. The experiments were conducted in three strongly water-wet carbonate rocks with different permeabilities. Experimental and numerical studies showed that the difference between co- and countercurrent flows was not significant because of air/brine interaction, which had a high viscosity ratio and almost zero fractional flow. In later studies, the researchers [164] conducted SI experiments for these three carbonates to examine the analytical equations of co/countercurrent imbibition and investigate the rate of water imbibition. The SI experiment was conducted by coating the lateral surface of the core and placing the dry core vertically into the imbibing water to mimic co-current water imbibition. Vertical orientation of the core can create gravity that affects water imbibition. However, the researchers calculated the gravitational pressure drop and found it did not exceed 0.44 psi, and the capillary pressure was much higher than the gravitational pressure for all three samples. The SI experiment was carried out between air and water, revealing that the water relative permeability and capillary pressure had a much greater effect on the analytical solutions. The rate of water imbibition was determined using the co-current imbibition test and the relative permeability and capillary pressure curves were calculated using the experimental and numerical results.

The authors of [159] also used the analytical solutions from [102] and compared them with a numerical simulator. They concluded that the analytical equation of co-current flow does not match with numerical models because of time scaling, which represents a limitation of the analytical equation. They examined the effect of gravity by changing the core orientation and using different wettability, along with different mobility ratios. The results of the numerical models showed that gravity can significantly affect the SI process and only the horizontal orientation of the core should be analyzed experimentally to avoid a mismatch with the analytical equations. The researchers also examined the effect of capillary back pressure on countercurrent flow, which can decrease oil production. Overall, they concluded that analytical solutions of co/countercurrent flows have some limitations and thus should be used with experimental measurements and commercial numerical simulators under proper guidelines and grid sensitivity analysis. Another approach to solving the analytical equation of countercurrent flow was proposed in [104]. The perturbation method was used in the numerical study, which was based on the integration of the diffusivity equation. Perturbation was found to be more straightforward than solving nonlinear integral equations.

Sections 5 and 6 of this article have given a general overview of the latest research to model fluid flow in NFR and LSW modeling. LSW involves geochemical and compositional modeling; wettability alteration is shown through relative permeability change by applying interpolation. There are numerous studies of simulation models for co/countercurrent flow applying different methods to solve analytical equations. Numerical studies can obtain relative permeability and capillary pressure curves of fractured formations, overcoming the time delay of long experimental studies. The SI process can be analyzed through co/countercurrent imbibition, which turns up detailed information about fracture-matrix interactions. However, these models provide an in situ water saturation profile only for simple black oil models, which are not reliable for LSW imbibition. LSW imbibition requires a dynamic wettability alteration process. There is no study yet in which dynamic wettability alteration is applied in analytical equations, even though wettability alteration is an important mechanism of the EOR methods in NFRs, which can increase oil production by changing the matrix wettability to a more water-wet state. It is essential to understand the fluid distribution between fracture and matrix as the composition of connate water and invading brine, which reacts with crude oil and rock surface, can differ. Further development of analytical solutions for LSW imbibition in NFRs can provide interesting information about the in situ water saturation profile, waterfront, and fluid distribution. Table 4 gives an overview of general research findings in the investigation of NFRs and further ways to develop the topic.

Table 4. Summary of experimental and numerical studies of LSW imbibition in NFRs and proposed research gaps and recommendations.

Available Studies	Findings	Research Gaps	Future Directions
Experimental Studies			
SI experiments on carbonate rocks to evaluate LSW performance and the effect of different parameters	Higher temperature leads to more recovery factors as the reaction rate increases (fast MIE) The occurrence of PDI in imbibing fluids increases oil production The presence of connate water has a positive effect on the SI process Higher permeability leads to faster SI.	The dominant mechanism of LSW that results in wettability alteration is still under research There are no general screening criteria for LSW imbibition	Requires more detailed studies, from the nanoscale to the macroscale, to identify the dominant mechanism These studies will add more experimental data to create screening criteria for carbonate rock

Table 4. Cont.

Available Studies	Findings	Research Gaps	Future Directions
Experimental Studies			
SI experiments with different boundary conditions on carbonate rock	Core length, gravity, IFT, initial wettability, connate water, porosity, and permeability temperature are analyzed during SI tests and their effect on co/countercurrent flows	Most works are conducted for AFO boundary conditions that do not separate co/countercurrent flows Most experiments are performed in vertical positions that create gravity TEO boundary condition does not separate co/countercurrent flows	An experimental setup should be created to separate co/countercurrent imbibition and eliminate the effect of gravity One end should be in contact with oil and the other one with water to create a co-current flow SI tests with different boundary conditions can be conducted to evaluate LSW performance
In situ water saturation measurements	Can give a unique solution for simulation models	Most are performed for the air–brine imbibition process There are no in situ water saturation measurements during LSW imbibition	Perform CT scanning for oil–brine SI test; LSW should be used as the imbibing fluid
Simulation Studies			
Analytical equations of co/countercurrent flow	Gives information about relative permeability and capillary pressure curves that take a long time to measure experimentally for NFRs	Some models are validated using others numerical models or SI tests between air and brine	Requires additional experimental measurements for validation Development of faster and more accurate numerical methods to solve equations
Geochemical modeling of LSW	Available software simulates LSW based on geochemical reactions and shows the interaction between crude oil, brine, and rock The basic principle is to show relative permeability and capillary pressure shift	Most of the models consider a waterflooding process of forced imbibition; NFRs require modeling of the SI process As the dominant mechanism is still unclear, it is difficult to identify the interpolation coefficient required to calculate relative permeability and capillary pressure	Modeling of SI process during LSW in available software
Modeling LSW in NFRs		Few examples provided of LSW imbibition in NFRs	Modeling LSW imbibition during the SI process and investigating dynamic wettability change through capillary pressure and relative permeability curves' shifting Understanding which parameter is more crucial in modeling the SI process during LSW imbibition
ML technique	Sensitivity analysis studies are conducted to evaluate LSW performance	There are lots of parameters that affect LSW and complex rock properties require more data to support good ML models	ML can be also used in analytical equations to solve differential equations

7. Conclusions

A review has been presented of the existing experimental and numerical studies of LSW imbibition in NFRs. NFRs have received great attention in research and academia due to their complex nature. The heterogeneity of the reservoir can result in an early breakthrough in waterflooding because most of the injected brine flows in the highly permeable fractures and most of the oil remains in the matrix. Understanding of the fracture-matrix interaction should be taken into consideration during reservoir development and future forecasting. Therefore, research on SI mechanisms and the development of analytical solutions for co/countercurrent flows is required to predict the performance of the fracture-matrix interaction and estimate relative permeability and capillary pressure values.

The wettability effect and wettability alteration process were analyzed in this critical review to reveal the importance of applying LSW injection in fractured reservoirs. Experimental and modeling studies showed the feasibility of the application of LSW injection in fractured formations.

Based on the critical review of LSW injection in NFRs, the following conclusions are presented:

- (1) The SI process consists of two flows that have different directions and can be measured experimentally by applying specific boundary conditions. Horizontal orientation must be applied to eliminate the effect of gravitational force and investigate only the capillary force, which is considered the main mechanism of oil displacement from the matrix. Use of the Bond number is proposed to investigate the effect of gravity, but it still requires more investigations that include IFT and other fluid/rock interactions in the porous media.
- (2) Another approach to investigating the SI process in the fracture-matrix interaction is to solve analytical equations based on diffusion. The diffusion coefficient is a function of the mobility ratios, capillary pressure, and saturation. The simulation studies showed that co-current flow results in higher and faster oil recovery than countercurrent flow. In addition, there is a strong dependence on wettability conditions, and the difference between the two flows becomes negligible as the rock is more oil-wet. There are some limitations of the simulation studies provided in the literature. Some of the works were validated using experimental data between air and water, which led to a high mobility ratio and extremely high capillary pressure. SI tests can be used for the validation of simulation data, but they can lead to non-unique solutions for the relative permeability and capillary pressure curves. A CT scan test can be used to measure the in situ water saturation distribution. However, the application of CT scans during SI tests is not always possible.
- (3) Most EOR techniques are intended to decrease the effect of the capillary pressure in mixed-wet or oil-wet fractured formations and rely on gravitational and viscous force alone. However, wettability alteration can offer another way to increase oil production. Changing the wettability from mixed-wet to a more water-wet state will increase the capillary-driven force in the fracture-matrix fluid movement. LSW can be used as a wettability modifier, which is considered an environmentally friendly and cheap EOR method.

8. Recommendations

According to the above-mentioned conclusions, the following recommendations are provided for further research development and studies:

- (1) It is recommended to conduct the experimental measurements of co/countercurrent imbibition with appropriate boundary conditions and horizontal orientation and/or the in situ water saturation distribution using a CT scan test, MRI, or NTI. Different parameters should be considered to investigate the performance of the SI process, such as the mobility ratio, shape factor, permeability, and original rock wettability.
- (2) The ML technique is used to evaluate the performance of LSW in sandstone and carbonates. No research has been found to evaluate NFRs and tight reservoirs using

ML. Further development of ML techniques in solving the differential equations can give us a chance of optimizing the analytical solutions of co/countercurrent imbibition and applying LSW imbibition in NFRs.

- (3) Experimental and simulation studies of LSW imbibition in fractured core samples have not yet been investigated very well and require more detailed attention. More advanced studies can be conducted such as CT scanning, MRI, and NTI to measure in situ water saturation distribution during LSW imbibition. Moreover, simulation models can include dynamic wettability alteration through changing relative permeability and capillary pressure curves. Simulation studies of LSW imbibition in NFRs can show in more detail the in situ water saturation profile, fluid distribution, and crude oil, rock, and brine interaction.

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Abbreviations

ANN	Artificial neural network
AFO	All faces open
DT	Decision tree
EDL	Electric double layer
EOR	Enhanced oil recovery
EW	Engineered water
HSW	High-salinity water
IFT	Interfacial tension
LSW	Low-salinity water
MIE	Multicomponent ionic exchange
MRI	Magnetic resonance imaging
NFR	Naturally fractured reservoir
NTI	Nuclear tracer imaging
OOCO	One open end and one isolated end
OOE	One open end
OOIP	Original oil in place
PDI	Potential determining ion
SI	Spontaneous imbibition
SVM	Support vector machine
SWCTT	Single-well chemical tracer test
TDS	Total dissolved solids
TEO	Two ends open
N_B	Bond number
C	Constant
φ	Porosity
σ	Surface tension
$\Delta\rho$	Density difference
g	Gravitational constant
k	Permeability of the medium
H	Height of the medium

q_t	Total flow rate
λ_w	Mobility of wetting phase, which is equal to $\frac{kk_{rw}}{\mu_w}$
λ_{nw}	Mobility of non – wetting phase, which is equal to $\frac{kk_{rnw}}{\mu_{nw}}$
λ_t	Total mobility, which is a ratio of non-wetting phase mobility to wetting phase mobility
P_c	Capillary pressure
k_r	Relative permeability
S_w	Water saturation
$D(S_w)$	Diffusivity coefficient
$f(S_w)$	Fractional flow of water
ω	Boltzmann variable
$k_{rw}^{altered}$	Calculated water relative permeability at each time step
$k_{ro}^{altered}$	Calculated oil relative permeability at each time step
k_{rw}^{HSW}	Water relative permeability of high-salinity water
k_{rw}^{LSW}	Water relative permeability of low-salinity water
k_{ro}^{HSW}	Oil relative permeability of high-salinity water
k_{ro}^{LSW}	Oil relative permeability of low-salinity water
$p_c^{altered}$	Calculated capillary pressure at each time step
p_c^{HSW}	Capillary pressure of high-salinity water
p_c^{LSW}	Capillary pressure of low-salinity water
τ_{kr}	Interpolation coefficient for relative permeability
τ_{P_c}	Interpolation coefficient for capillary pressure

Appendix A

Table A1. Experimental studies of LSW imbibition in carbonates.

Author(s)	Core Properties	Brine	Oil	Core Wettability	Imbibition Temperature	Investigated Parameters	Results
[165]	Stevns Klint chalk outcrop $\Phi = 45\text{--}50\%$ $K = 2\text{--}5$ mD $L = 7$ cm $D = 3.75$ cm	Seawater (SW)— Modified SW with various $[\text{SO}_4^{2-}]$	Crude oil A (AN = 2.07 mg KOH/g) Crude oil B (AN = 0.55 mg KOH/g)	Moderate water-wet to preferential oil-wet	70 °C 100 °C 130 °C (Each test is performed at these temperatures from start)	$[\text{SO}_4^{2-}]$	40–45% OOIP additional oil recovery as $[\text{SO}_4^{2-}]$ increases from 0 to 0.096 mol/L (4 times SW concentration)
						Temperature	12% OOIP more oil recovery as temperature increases from 70 °C to 130 °C
[126]	Stevns Klint chalk outcrop $\Phi = 47\text{--}50\%$ $K = 2\text{--}4$ mD $L = 6\text{--}7$ cm $D = 3.7$ cm	Seawater (SW)— Modified SW with various $[\text{Ca}^{2+}]$	Crude oil (AN = 2.07 mg KOH/g)	Preferential water-wet	40 °C → 70 °C → 100 °C → 130 °C (T increased one after another, not from the start)	$[\text{Ca}^{2+}]$ Temperature	3–5% OOIP additional oil recovery as $[\text{Ca}^{2+}]$ increases from 0.058 to 0.232 mol/L in initial brine and from 0 to 0.052 in imbibing brine at 70 °C and 100 °C No additional oil recovery as $[\text{Ca}^{2+}]$ increases at low T (40 °C) 6% OOIP less oil recovery as $[\text{Ca}^{2+}]$ increases at high T (130 °C) due to CaSO_4 precipitation

Table A1. Cont.

Author(s)	Core Properties	Brine	Oil	Core Wettability	Imbibition Temperature	Investigated Parameters	Results
[127]	Stevns Klint chalk outcrop $\Phi = 45\text{--}50\%$ $K = 2\text{--}5$ mD $L = 7$ cm $D = 3.7$ cm	Seawater (SW)— Modified SW with various $[\text{SO}_4^{2-}]$, $[\text{Ca}^{2+}]$, and $[\text{Mg}^{2+}]$	Crude oil A (AN = 2.07 mg KOH/g) Crude oil B (AN = 0.55 mg KOH/g)	Moderate water-wet	40 °C $\rightarrow$ 70 °C $\rightarrow$ 100 °C $\rightarrow$ 130 °C (T increased one after another, not from the start)	$[\text{SO}_4^{2-}]$	35% OOIP additional final oil recovery as $[\text{SO}_4^{2-}]$ increases from 0 to 0.096 mol/L (4 times SW concentration) while Mg^{2+} is added after 53 days
						$[\text{Ca}^{2+}]$ and $[\text{Mg}^{2+}]$ Temperature	30% and 15% OOIP additional final oil recovery as $[\text{Ca}^{2+}]$ and $[\text{Mg}^{2+}]$ increase from 0 to 0.045 at 40 °C $\rightarrow$ 70 °C, respectively 37% and 29% OOIP additional final oil recovery as $[\text{Mg}^{2+}]$ and $[\text{Ca}^{2+}]$ increase from 0 to 0.045 at 70 °C $\rightarrow$ 100 °C $\rightarrow$ 130 °C, respectively
[88]	Stevns Klint chalk outcrop $\Phi = 45\text{--}50\%$ $K = 2\text{--}5$ mD $L = 4\text{--}5, 7$ cm $D = 3.7$ cm	Ekofisk formation water (FW)— Seawater (SW)— Modified SW (SW4S) with 4 times $[\text{SO}_4^{2-}]$	Crude oil A (AN = 2.07 mg KOH/g) Crude oil C (AN = 0.49 mg KOH/g)	Preferential oil-wet	50 °C 130 °C	Top end open (countercurrent)— both ends open (both co- and countercurrent)	14% and 8% OOIP additional oil recovery for both ends open cases compared to the only top end open case by SI of SW and SW4S, respectively
						$[\text{SO}_4^{2-}]$	8% OOIP additional oil recovery by SW compared to FW with no $[\text{SO}_4^{2-}]$ 9–15% OOIP additional oil recovery by SW4S compared to SW
						S_{wc}	10% OOIP greater oil recovery difference between top and bottom surfaces in both ends open case as connate water saturation increases from 0 to 25.7%
						Core length	7% OOIP more oil recovery difference between top and bottom surfaces in both ends open case as core length increases from 4 to 7 cm

Table A1. Cont.

Author(s)	Core Properties	Brine	Oil	Core Wettability	Imbibition Temperature	Investigated Parameters	Results
[120]	Reservoir limestone core $\Phi = 30\%$ $K = 53$ and 78 mD $L = 4.9$ cm $D = 3.8$ cm	SW—SW0S— SW3S	Stock tank oil (AN = 0.05 mg KOH/g)	Aging for 4 weeks at 90°C	120°C	$[\text{SO}_4^{2-}]$	15% OOIP additional oil recovery by SI of SW compared to SW0S without SO_4^{2-} No additional oil recovery by SI of SW3S due to CaSO_4 precipitation
[166]	Stevns Klint chalk outcrop $\Phi = 45\text{--}50\%$ $K = 2\text{--}5$ mD $L = 3.5\text{--}4.5$, 7 cm $D = 3.7$ and 3.8 cm	Ekofisk formation water (FW) —Seawater (SW)	Crude oil A (AN = 2.07 mg KOH/g) Crude oil C (AN = 0.49 mg KOH/g)	Preferential oil-wet	50°C 130°C	$[\text{SO}_4^{2-}]$	7–8% OOIP additional oil recovery by SW compared to FW with no $[\text{SO}_4^{2-}]$ at 130°C
						S_{wc}	No major effect on final oil recovery as S_{wc} increases from 0 to 25.7% (40–50% OOIP for both) 6–8% OOIP additional oil recovery from the top surface as S_{wc} increases from 0 to 25.7% 4–6% OOIP less oil recovery from the bottom surface as S_{wc} increases from 0 to 25.7%
						Core length	10–15% OOIP additional oil recovery as core length increases from 3.5 to 7 cm for only top end open at 130°C
[121]	Middle East reservoir limestone core (microcrystalline LS) $\Phi = 29\%$ $K = 3$ mD	Formation water (FW)—aquifer brine LS1— $[\text{SO}_4^{2-}] = 1.8$ g/L— Modified aquifer brine LS2 $[\text{SO}_4^{2-}] = 4.1$ g/L— Modified aquifer brine LS3 $[\text{SO}_4^{2-}] = 9.5$ g/L)	Crude oil	Aging with crude oil	60°C	$[\text{SO}_4^{2-}]$ to $[\text{Ca}^{2+}]$ ratio	4–5% OOIP additional oil recovery as the imbibing brine switches from FW to sulfate-enriched LS2 and LS3 with sulfate-to-calcium ratios of 8.2 and 27.3 No additional oil recovery by SI of LS1 with sulfate-to-calcium ratio of 2.73 compared to FW imbibition

Table A1. Cont.

Author(s)	Core Properties	Brine	Oil	Core Wettability	Imbibition Temperature	Investigated Parameters	Results
[167]	Reservoir limestone core $\Phi = 13\text{--}17\%$ $K = 0.3\text{--}1$ mD $L = 5.22\text{--}8.31$ cm $D = 3.8$ cm	Formation water (FW)—High-salinity seawater (HSSW)—Manipulated HSSW (HSSW0NaCl and HSSW4S0NaCl)	Crude oil N (mixing four different oils) (AN = 0.08 mg KOH/g)	Preferential water-wet	110 °C	[SO ₄ ^{2−}] and [NaCl] Secondary imbibition of FW	13%, 7%, and 6% OOIP additional oil recovery by tertiary imbibition of HSSW-0NaCl, HSSW, and HSSW-4S compared to FW secondary SI, respectively
						Secondary imbibition of HSSW	No incremental oil recovery by secondary SI of HSSW compared to secondary SI of FW (approximate 40% OOIP oil recovery for both)
[168]	Stevns Klint chalk, Rørdal chalk, and Niobrara chalk outcrops $\Phi = 40\text{--}50\%$ $K = 2\text{--}5, 3\text{--}8$, and $0.1\text{--}3$ mD, respectively $L = 6$ cm $D = 3.8$ cm	Formation water (FW)—Seawater (SW)—Manipulated SW (SW0S and SW4S)	Crude oil (AN = 0.41 mg KOH/g)	Strongly water-wet	130 °C	[SO ₄ ^{2−}]	6.5–35% OOIP additional oil recovery for Stevns Klint chalk cores as [SO ₄ ^{2−}] increases from 0 to 0.094 (4 times SW) for different Amott water indices (I_w)
						Initial wettability	19% OOIP additional final oil recovery by SW4S SI as water Amott index (I_w) decreases from 0.23–0.31 to 0.08–0.14 (changes toward less water-wetness)
						Chalk type	No added oil recovery as increasing [SO ₄ ^{2−}] in aged Rørdal and Niobrara chalk core plugs
[169]	Stevns Klint chalk outcrop, Silurian dolomite outcrops, 3 reservoir limestone cores, reservoir dolostone core $\Phi = 17\text{--}50\%$ $K = 2\text{--}235$ mD	FW—synthetic seawater (SSW)—Wettability modifying (WM) waters with different ionic strengths and [SO ₄ ^{2−}]	Crude oil A (AN = 0.9 mg KOH/g) Crude oil B (AN = 0.4 mg KOH/g) Crude oil C (AN = 0.07 mg KOH/g)	Aging for 4 weeks at reservoir temperature	60 °C 70 °C 85 °C 120 °C (each T for specific carbonate types)	[SO ₄ ^{2−}] and ionic strength Carbonate type	5–15% OOIP additional oil recovery as SO ₄ ^{2−} concentration increases from 0.002 to 0.019–0.099 mol/L in Stevns Klint chalk outcrops 4–20% OOIP additional oil recovery by decreasing ionic strength

Table A1. Cont.

Author(s)	Core Properties	Brine	Oil	Core Wettability	Imbibition Temperature	Investigated Parameters	Results
[123]	Reservoir core from Oman (98.5% calcite + dolomite) $\Phi = 22\text{--}26\%$ $K = 3\text{--}4$ mD $L = 4.6\text{--}4.9$ cm $D = 3.8$ cm	Synthetic brine—2-, 5-, 10-, and 100-times diluted brine (used one after another)	Dead crude oil	Aging for 20–30 days	70 °C	Dilution	16–20% additional oil recovery as the dilution ratio increases from 0 to 2–100
[170]	Reservoir limestone core from UAE $\Phi = 19.5\%$ $K = 1.15$ mD $L = 6.81$ cm $D = 3.85$ cm	Seawater (SW)—40 times diluted SW (40DSW)	Stock tank crude oil	Mixed-wet	70 °C	Dilution	18.4% OOIP additional oil recovery as imbibing brine switches from SW to 40DSW
[171]	Silurian dolomite outcrop $\Phi = 20\%$ $K = 201\text{--}235$ mD $L = 4.97$ cm $D = 3.77$ cm	FW—SW—10 times diluted seawater (10DSW)—100 times diluted formation water (100DFW)	Crude oil (AN = 0.52 mg KOH/g)	Slightly water-wet	70 °C	Dilution	1–3% OOIP additional oil recovery as imbibing brine switches from FW to SW 10–15% OOIP additional oil recovery as imbibing brine switches from SW to 10DSW No enhanced oil recovery for 100DFW without sulfate
	Stevens Klint chalk outcrop $\Phi = 45\text{--}50\%$ $K = 1\text{--}3$ mD $L = 7$ cm $D = 3.77, 3.8$ cm	FW with different individual $[\text{Ca}^{2+}]$ and $[\text{Mg}^{2+}]$ —NaCl imbibing brine	Crude oil A (AN=0.34 mg KOH/g) Crude oil B (AN = 0.17 mg KOH/g)	Preferential water-wet	25 °C	$[\text{Ca}^{2+}]$ and $[\text{Mg}^{2+}]$	3% OOIP less oil recovery (less water-wetness) as $[\text{Ca}^{2+}]$ in the FW increases from 0.046 to 0.566 mol/L 5% OOIP more oil recovery (more water-wetness) as $[\text{Mg}^{2+}]$ in the FW increases from 0.054 to 0.66 mol/L

Table A1. Cont.

Author(s)	Core Properties	Brine	Oil	Core Wettability	Imbibition Temperature	Investigated Parameters	Results
[172]	Indiana limestone core $\Phi = 17.49\text{--}19.29\%$ $K = 101.26\text{--}212.08$ mD $L = 6.98\text{--}7.64$ cm $D = 3.845$ cm	100 times diluted formation water (100DFW)—100 times diluted FW with 5, 10 times $[\text{Mg}^{2+}]$, $[\text{SO}_4^{2-}]$ individually as well as in combination (100DFW-5M) (100DFW-10S) (100DFW-5M-10S)	Crude oil from Oman carbonate reservoir (AN = 0.37 mg KOH/g)	Mixed-wet or oil-wet	75 °C	Dilution	50% OOIP additional oil recovery as imbibing brine switched from FW to 100 times diluted FW
						$[\text{Mg}^{2+}]$, $[\text{SO}_4^{2-}]$	2% OOIP less oil recovery as imbibing brine switched from 100 times diluted FW to 100 times diluted FW spiked with 5 times $[\text{Mg}^{2+}]$ 7, 17% OOIP additional oil recovery as imbibing brine switched from 100 times diluted FW to 100 times diluted FW spiked with 10 times $[\text{SO}_4^{2-}]$ /combination of 10 times $[\text{SO}_4^{2-}]$ and 5 times $[\text{Mg}^{2+}]$, respectively
[173]	Carbonate core (73% calcite) $\Phi = 19\%$ $K = 32$ mD $L = 6.7$ cm $D = 3.81$ cm	5 times diluted seawater (5DSW)—Smart seawater with manipulated $[\text{SO}_4^{2-}]$, $[\text{Ca}^{2+}]$, and $[\text{Mg}^{2+}]$ (SW-3S-C-3M)	Crude oil (southern Iranian fractured carbonate)	Aging for 40 days at 75 °C	75 °C	Dilution Smart seawater	9% OOIP additional total oil recovery by SI of SSW compared to 5DSW due to the presence of sulfate for the TOF case
						Boundary condition One open face (OOP)—Two open faces (TOF)—One open face and another face isolated from brine (OOCO)	9–12% and 18–23% OOIP additional oil recovery for TOF case compared to one OOF or OOCO, respectively, due to the simultaneous co- and countercurrent imbibition
[174]	Reservoir limestone core (98–100% calcite, 0–2% quartz) $\Phi = 15\text{--}25\%$ $K = 2\text{--}20$, 20–400 mDL = 5 cm $D = 3.8$ cm	Formation water (FW)—Seawater (SW)—5- and 10-times diluted SW (5DSW and 10DSW)	Stock tank crude oil	Mixed-wet or oil-wet	70 °C	Dilution Secondary (in each brine from the start of the test) and tertiary (one after another) modes	12% and 8% OOIP additional oil recovery by SI of 10DSW compared to FW and SW, respectively, in secondary mode 5% OOIP additional oil recovery by SI of SW compared to FW in tertiary mode 2% OOIP additional oil recovery by SI of 5DSW compared to SW in tertiary mode

Table A1. Cont.

Author(s)	Core Properties	Brine	Oil	Core Wettability	Imbibition Temperature	Investigated Parameters	Results
[128]	Carbonate reservoir core (94% calcite, 6% dolomite) $\Phi = 17\text{--}20\%$ $K = 0.4$, 2–3 and 182 mD $L = 4\text{--}5$ cm $D = 3.8$ cm	Persian Gulf seawater (SW)—5-, 10-, 20-, and 40-times diluted SW (5DSW, 10DSW, 20DSW, and 40DSW)	Dead crude oil (AN = 0.1 mg KOH/g)	Mild oil-wet	35 °C 55 °C 75 °C	Dilution	12% and 2.5% OOIP additional oil recovery by SI of 20DSW compared to distilled water and 40DSW, respectively
						Core permeability	15% OOIP additional oil recovery as core permeability increases from 2.46 to 182.25 mD
						S_{wc}	14% OOIP additional oil recovery as S_{wc} increases from 0 to 25%
						Temperature	1.5% OOIP additional oil recovery as T increases from 35 °C to 55 °C 10% OOIP additional oil recovery as T increases from 55 °C to 75 °C
[175]	Carbonate reservoir core from the south of Iran $\Phi = 18\%$ $K = 2.5$ mD $L = 5.5$ cm $D = 3.7$ cm	SW—Modified SW with manipulated $[\text{SO}_4^{2-}]$, $[\text{Ca}^{2+}]$, $[\text{Mg}^{2+}]$, $[\text{Na}^+]$, and $[\text{Cl}^-]$	Crude oil from an oil field in the south of Iran (AN = 0.38 mg KOH/g)		25, 70, and 90 °C	Temperature	14–18 % OOIP additional oil recovery as T increases from 70 °C to 90 °C for modified SW solutions
						$[\text{SO}_4^{2-}]$, $[\text{Ca}^{2+}]$, $[\text{Mg}^{2+}]$, $[\text{Na}^+]$, and $[\text{Cl}^-]$	10, 5, 4, and 2% OOIP additional oil recovery by SI of SW with 3 times $[\text{SO}_4^{2-}]$, without $[\text{Na}^+]$ and $[\text{Cl}^-]$, 3 times $[\text{Mg}^{2+}]$, and 3 times $[\text{Ca}^{2+}]$ compared to SW, respectively
[176]	Indiana limestone outcrop $K = 4\text{--}8.6$, 8–15 mD $L = 5\text{--}9$ cm $D = 3.81$ cm	High-salinity formation water (FW)—Seawater (SW)—100 times diluted SW (100DSW)	Dead crude oil	Aging for 30 days at 90 °C	70 °C	Dilution Salinity difference between connate water (CW) and imbibing water (IW)	1–3% OOIP additional oil recovery as long as there is no salinity difference 13% OOIP additional oil recovery by SI of 100DSW compared to sulfate-rich SW in the case of FW as CW No oil production by SI of FW and SW in the case of 100DSW as CW

Table A1. Cont.

Author(s)	Core Properties	Brine	Oil	Core Wettability	Imbibition Temperature	Investigated Parameters	Results
[177]	Carbonate reservoir core $\Phi = 13\text{--}17\%$ $K = 6\text{--}19$ mD $L = 5\text{--}9$ cm $D = 3.81$ cm	FW, SW, and SW with manipulated $[\text{SO}_4^{2-}]$, $[\text{Ca}^{2+}]$, and $[\text{Mg}^{2+}]$ (SW, SW-2C, SW-2M, SW-2S, SW-4S)	Dead oil (AN = 0.07 mg KOH/g)	Partially oil-wet	25 °C → 45 °C → 55 °C → 70 °C (T increased one after another, not from the start)	$[\text{SO}_4^{2-}]$, $[\text{Ca}^{2+}]$, and $[\text{Mg}^{2+}]$	1–2% OOIP additional oil recovery by SI of smart water with the highest sulfate content (SW-4S) compared to SW-2S
						Temperature	7, 3.5, and 5.5% OOIP additional oil recovery as temperature increased to 45, 55, and 70 °C, respectively, for SW-4S smart SW
[178]	Reservoir core plug $\Phi = 15.5\text{--}17.5\%$ $K = 2\text{--}3$ mD $L = 7.9\text{--}8.3$ cm $D = 3.7$ cm	SW and modified SW with manipulated $[\text{SO}_4^{2-}]$, $[\text{Ca}^{2+}]$, and $[\text{Mg}^{2+}]$	Dead oil (AN = 2.9 mg KOH/g)	Aged in crude oil for 6 weeks at 60 °C	40 and 60 °C	Temperature	2–6% OOIP additional oil recovery by increasing the temperature to 60 °C
						$[\text{SO}_4^{2-}]$, $[\text{Ca}^{2+}]$, and $[\text{Mg}^{2+}]$	6, 7, and 5% OOIP additional oil recovery by SI of SW with 2 times $[\text{Ca}^{2+}]$, 2 times $[\text{SO}_4^{2-}]$, and 3 times $[\text{Mg}^{2+}]$, respectively, compared to SW
[98]	Carbonate core (73% calcite) $\Phi = 15\text{--}24\%$ $K = 25\text{--}33$, 72 mD $L = 5\text{--}9$ cm $D = 3.81$ cm	5 times diluted seawater (5DSW)—Smart seawater with manipulated $[\text{SO}_4^{2-}]$, $[\text{Ca}^{2+}]$, and $[\text{Mg}^{2+}]$ (SW-3S-C-3M)	Crude oil (southern Iranian fractured carbonate)	Aging for 20 days at 75 °C	70 °C	Dilution Smart seawater	9% OOIP additional total oil recovery by SI of SSW compared to 5DSW because of sulfate for TOF case
						Boundary condition One open face (OOP)—Two open faces (TOF)—One open face and another face isolated from brine (OOCO)	9–12% and 18–23% OOIP additional oil recovery for TOF case compared to one OOF and OOCO, respectively, due to the simultaneous co- and countercurrent imbibition
						Core permeability	8% total production (5% OOIP) additional countercurrent flow as permeability increases from 33 to 72 mD
						Core length	13% and 23% total production (6% and 12% OOIP) additional countercurrent flow as core length increases from 5 to 7 or 9 cm, respectively

Table A1. Cont.

Author(s)	Core Properties	Brine	Oil	Core Wettability	Imbibition Temperature	Investigated Parameters	Results
[179]	Limestone outcrop $\Phi = 15\text{--}20\%$ $K = 30\text{--}53$ mD $L = 4.6$ cm $D = 3.7\text{--}3.8$ cm	Synthetic SW and diluted SW with manipulated $[\text{SO}_4^{2-}]$, and $[\text{Mg}^{2+}]$	Dead crude oil (AN = 3.30 mg KOH/g)	Aging for 14–90 days at 96 °C	96 °C	Dilution	No response to improved oil recovery
						$[\text{SO}_4^{2-}]$, $[\text{Mg}^{2+}]$	3% OOIP additional oil recovery as $[\text{SO}_4^{2-}]$ increases from 2 to 4 times 10% OOIP additional oil recovery as $[\text{Mg}^{2+}]$ increases from 4 to 8 times in a low NaCl environment
[180]	Brazilian pre-salt rock samples $\Phi = 14\text{--}28\%$ $K = 286\text{--}1250$ mD $L = 4\text{--}6$ cm $D = 3.75\text{--}3.80$ cm	FW, SW, and modified SW with copper	Crude oil with 7.47 cP viscosity	Aging for 15 days at 63 °C	63 °C	$[\text{NaCl}]$, $[\text{Ca}^{2+}]$, $[\text{Mg}^{2+}]$, and $[\text{CuCl}_2]$	19.4% OOIP additional oil recovery from the total reduction in NaCl from the SW spiked with 1 g/L of CuCl_2 in secondary mode 3.9% OOIP additional oil recovery by SW without PDIs and with CuCl_2 and reduced sulfate content in tertiary mode

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