INTRODUCTION

LSWI is a subject which has been proposed by Morrow and his research colleagues during their studies on Crude Oil/Brine/Rock (COBR) in early 90s while working on wettability alteration; although having been proposed for more than 30 years (Dang et al., 2015a), it is only in the past decade that special attention has been spent on it as this method proved efficient by many field studies (Jadhunandan and Morrow, 1995; Tang and Morrow, 1999; Drummond and Israelachvili, 2002; McGuire et al., 2005; Lager et al., 2008a, 2008b; Vledder et al., 2010; Skrettingland et al., 2011; Thyne et al., 2011; Zekri et al., 2012; Shabib-Asl et al., 2014a).

Determining the effectiveness of LSWI in carbonate rocks and its impacting factors are crucial since 60% of total world oil reserves are in carbonates. In case of carbonate reservoirs since they are usually oil-wet or mixed-wet, water flooding is not an efficient recovery method because imbibition is low, leaving 80% of the Original Oil in Place (OOIP) upswept (Chen and Mohanty, 2014). In such cases LSWI can increase the recovery (Cissokho et al., 2010; Vledder et al., 2010; Chen and Mohanty, 2014; Attar and Muggeridge, 2015; Dang et al., 2015a; Mahani et al., 2015a, 2015b).

Injecting Low Salinity Water (LSW) to increase oil recovery has been investigated in both carbonates and sandstone rocks (Bagci et al., 2001; Al-Aulaqi et al., 2013). Despite the wide applications of LSW injection in both of the cases, the actual mechanism behind LSW is yet to be identified (Cissokho et al., 2010; Al-Attar et al., 2013; Rotondi et al., 2014; Mahmoud and Abdelgawad, 2015). The complexities linked to understand the mechanism of carbonates are even more due to factors such as the rock’s heterogeneity (Al-Shalabi et al., 2015a), though in both case of sandstones and carbonate rocks the mechanism is said to be linked with wettability (Zekri et al., 2012; Alameri et al., 2015).

Wettability characteristic of the reservoir is reportedly controlled by brine ion such as Ca$^{2+}$, Mg$^{2+}$ and SO$_4^{2-}$, so that brine ion optimization can dedicate to enhancing oil recovery (Tang and Morrow, 1999; Zhang and Morrow, 2006; Fathi et al., 2010). In a study by Zhang et al. (2007) it is shown that increasing
calcium ion concentration in the brine solution causes enhancement in oil recovery. In a similar study the same effect is observed for an optimum SO$_4^{2-}$ concentration in carbonate rocks (Awolayo et al., 2014).

The present study reviews the results and achievements of recent researches on LSWI. However the Mechanism of LSWI and role of brine ions (Ca$^{2+}$, Mg$^{2+}$ and SO$_4^{2-}$) are not clear. The researchers did not give holistic view of the role of brine ions from the LSWI perspective. This research, therefore, provides recent and different viewpoints on LSWI, wettability alteration and role of brine ions. Introducing new and effective method in order to gain desire results for future is presented in last part of research.

**Mechanisms of LSWI:** As the actual mechanism behind LSW has not been scientifically defined, there are many different contradictory hypotheses which contribute to the explanation of the mechanism. Some of these theories are fines migration/mineral dissolution, Multi-component Ionic Exchange (MIE), pH modification, limited release of mixed-wet particles; emulsification; saponification; surfactant-like behavior; double layer effects; salt-in effects; osmotic pressure and wettability alteration (Dang et al., 2015b).

In mineral adsorption theory, the main contributing factor to LSWI is identified to be mineral cation adsorption to clay (Jabbar et al., 2013). A chain reaction between the water and cation (Ca$^{2+}$ or Mg$^{2+}$) leads to acid production, water adsorption to the clay surface through acidic head since the surface is originally positively charged, which increases water-wetness of the reservoir and consequently dedicating to enhancing oil recovery (Austad et al., 2010). However in contradictory results, the validity of this theory is questioned as in LSWI, the pH does not drop enough to dedicate to such acidity change (Lager et al., 2008a; Rivet, 2009; Fjelde et al., 2012).

In double Layer Effect the rock-liquid forces are studied; according to this theory, the Van der Waals attraction combined with electrostatic repulsion improves water wettability through reduction between clay-clay attraction forces (Sheng, 2014). According to Nasralla et al. (2011) COBR interactions produces repulsive electrical forces in double layer which helps stabilize the water film, increasing water wetness of the reservoir (Chakravarty et al., 2015).

One of the important factors in LSWI is ionic exchange, mechanism of which depends on involved compositions. It is bases on ionic exchange theorem that ions adsorb to solid rock surface at the place of being effluent in liquid phase, disturbing the existing thermodynamic equilibrium (Chakravarty et al., 2015). This is why in laboratory scales where the oil sample used is refined oil, which does not have enough polar compounds, no ionic exchange occurs and LSWI is not beneficial (Strand et al., 2003; Hirasaki and Zhang, 2004; Sheng, 2014), based on this simple fact, there is direct relationship between the Acid Number (AN) and LSWI effectiveness (Zhang and Austad, 2005).

As for pH theories, increasing acidity due to calcite and dolomite dissolution in the formation water produces the ions necessary to involve in exchange and on the same basics as for ionic exchange theorem, LSWI mechanism enforces (McGuire et al., 2005; Rivet, 2009; Austad et al., 2010; Hiorth et al., 2010; Evje and Hiorth, 2011; Fjelde et al., 2012). On the other hand, calcite dissolution widens the pores by connecting the small and bigger pores, which will allow more flow and increases recovery from the reservoir (Yousef et al., 2011a). Although, Mahani et al. (2015b) concluded that mineral dissolution effect is only applicable in case of laboratory scale and does not apply for reservoir condition.

In a new study (Dang et al., 2015b) a clay distribution model is proposed for LSWI base on the results from which, for higher amount of Ca$^{2+}$ and Mg$^{2+}$, ionic exchange rate in the environment, is higher, so that wettability alteration is more and oil recovery increases. In the Fig. 1, MIE is compared with Ionic Exchange (IE) during surfactant flooding. As it can be seen oil recovery by MIE mechanism is always higher than IE which identifies the importance of MIE above in general IE. Also in term of timing, a long term flooding schedule shows higher values for both IE and MIE mechanism.

**Wettability alteration:** Wettability is a function of reservoir parameters such as rock type, fluid type (oil, water, gas) and also reservoir temperature. Since these parameters vary from one reservoir to another, the upcoming results for different investigations are different. For instance, considering wettability mechanism in carbonate rocks and sand stones, carbonates have positive charges on their surface while sandstones are negatively charged, leading to different rock interactions with the ionic environment surrounding them, each. A correct analysis of wettability alteration mechanism in reservoir is not achieved unless parameters to which it depends on is determined and understood.
Maybe the most debatable LSWI mechanism is wettability alteration since the actual reasons behind its process is of argument (Zahid et al., 2012). A couple of factor influence wettability some of which are ion exchange (Lager et al., 2008b; Austad et al., 2011), geochemical reactions, dissolution/fine migration (Tang and Morrow, 1999; Hiorth et al., 2010), surface charge alteration, in-situ surfactant generation, or a combination of the named factors (Al-Shalabi et al., 2015a).

On the other hand, applying wettability alteration determination methods such as contact angle measurement and zeta potential during LSWI, it is confirmed that wettability alteration is the main factor dedicating to enhance oil recovery in both of sandstone and carbonates cases, increasing recovery 5% to 40% in different cases (Nasralla et al., 2011; Yousef et al., 2011b; Mohanty and Chandrasekhar, 2013; Jabbar et al., 2013; Chen and Mohanty, 2015; Kafili Kasmaei and Rao, 2015; Qiao et al., 2015; Sánchez-Rodríguez et al., 2015).

In different studies conducted on chalk and limestone rocks, it was reported that wettability alteration toward a water-wet condition caused by Potential Determining Ions (PDI) is the main factor changing recovery from low to higher values (Austad et al., 2005; RezaeiDoust et al., 2009).

In similar experiment on chalk, samples exposed to seawater showed less oil-wet characteristic caused by ionic adsorption/exchange between brine ions to rock surface, which induced imbibition process and finally increased the overall recovery (Kleppe et al., 2013). According the results reported by Yousef et al. (2011a), a combination of ionic exchange, enhanced sulfate concentration in the injective brine phase and mineral dissolution is the mechanism behind LSWI enhanced oil recovery.

Wettability alteration mechanism: In case of carbonate reservoirs, a suitable replacement for water flooding is surfactant flooding. During surfactant flooding, together with wettability alteration, relative permeability and residual saturation of the involved phases, as well as the capillary pressure also change (Kalaei et al., 2013). In a microscopic, COBR ionic exchange occurs between the oil’s carboxyl group (R-COO-) where the brine ions, namely Ca$^{2+}$ and Mg$^{2+}$ attract the carboxyls and on the other hand between the brine ions and carbonate surface where the same attraction adsorbs SO$_4^{2-}$ from the brine ions to the carbonate surface which alters the existing oil-wet condition of the carbonates towards water-wet through pH alteration (Austad et al., 2011).

Many other researchers have come to the same conclusion that the involving ions in the ionic exchange process in carbonate LSWI are calcium, Magnesium and sulfate (Tang and Morrow, 1999; Strand et al., 2003; Austad et al., 2005; Strand et al., 2006; Zhang et al., 2007; Mohanty and Chandrasekhar, 2013; Dang et al., 2015b). There is a repulsive force between the liquid phase’s interfaces in the reservoir, which applying LSWI intensifies. The increases repulsion stabilizes the water layer between the oil-brine and brine-surfactant and as water wettability increase; oil recovery enhances (Sheng, 2010). A detailed schematic of the process is illustrated in the Fig. 2 (Qiao et al., 2015).

According to the Fig. 2, COBR interaction, considering a small portion of the surface where all existing phases are at equilibrium. The surfactant acts as a bridge between the two phases of oil and water, from one head (Anion tail) the surfactant connects to oil and from the other side it is connected to water phase. Sulfate group from the brine connects to carboxyl group from the oil phase. On the other hand carboxyl group after dissociating from the rock dissolution reconnects
the brine cations (Lichtner, 1996; Langmuir et al., 1997).

The two crucial cations involved in the wettability reduction behave differently; Mg\(^{2+}\) behaves solely, meaning it gets adsorbs alone while Ca\(^{2+}\) is accompanied by carboxyl ion (Chakravarty et al., 2015).

Although the proposed mechanism involving the named cations is believed to be responsible for wettability alteration in chalk-carbonate rocks, as much as the wettability mechanism is controversial, this argument cannot be utilized for all cases solely. Experimental studies undertaken by Fernø et al. (2011) and Maevskyi (2014) is a proof for this claim.

Investigations on effect of temperature and concentration of ions on improving LSWI oil recovery by Austad et al. (2005) propose a direct relationship between both factors and oil recovery in understudied chalk rocks (Al-Hashim et al., 2015). Studies by Strand et al. (2008) also verify the same results, relating wettability alteration to activation energy of the involved chemical elements, which is directly proportional to temperature.

Amongst the responsible ions for wettability alteration, sulfate ion is the most dedicating. According to investigations, sulfate ion has the highest impact on wettability reduction in case of carbonate rocks, while experiments using calcite also shows the same impact for an optimized sulfate concentration, after which wettability changes cannot be related to sulfate ion. According to the same study, the best case if wettability alteration is observed when SO\(_4^{2-}\) and Ca\(^{2+}\) have the highest possible concentration, considering mixing them in a way that causes no precipitation (Jabbar et al., 2013).

On the impact and mechanism of Mg\(^{2+}\) and Ca\(^{2+}\), calcium ions adsorb to the surface immensely since their electrostatic repulsive force reduces more dramatically and so their reactivity to carboxyl group increase, which is also the reason why calcium and carboxyl are found together; while magnesium dedicates to wettability alteration mechanism in higher temperatures only (T>90°C to 100°C) due to dehydration (Zhang and Austad, 2005; Zhang and Austad, 2006; Zhang et al., 2007; RezaeiDoust et al., 2009; Zekri et al., 2012).

New attributes to Wettability alteration and LSW:
Modeling LSWI and wettability alteration processes are a new subject of attention. Although determining all the involved processes requires a fair understanding of the mechanism behind wettability alteration, applying models with capabilities of stimulating the related COBR interactions between the involved phases can dedicate to achieve the objectives of this study.

As the involved COBR interaction are crucially important to understand the correct mechanism of wettability alteration and since such behaviors are difficult to predict, simulation through numerical and experimental modeling have been proposed ref(Qiao et al., 2015).

In a new study by Texas university researches (Delshab et al., 2009; Al-Shalabi et al., 2015b; Tavassoli et al., 2015) put forward University Of Texas Chemical Simulator (UTCHEM) which is a reservoir geochemical simulator with abilities to predict chemical processes, including surfactant flooding, in a cost and time effective manner. According to the results from the simulation, wettability alteration was successfully validated identifying matrix properties as the main contributor to imbibition which consequently brings about the preferred wettability alteration. Other software include CMG’s CMOST™ which not only are used for history matching to validate the field and theory data, but also can help optimize LSWI (Dang et al., 2015a). In case of numerical modeling, simulating LSWI determining two factors are important; the chemical composition of the injection and also well placement in order to achieve a desirable wettability and successful flooding. An increase in oil recovery is associated with a good LSWI modelling, which itself is dependent on geological factors (Dang et al., 2015a).

**DISCUSSION**

**Low salinity surfactant flooding:** Surfactant flooding with the goal of reducing Interfacial Tension (IFT) and wettability alteration to increase the recovery factor from the reservoir is the topic of interest for many researches.

One of the surfactant’s disadvantages is its high cost which makes it economically infeasible, which on the other hand is a constraint to its useful application as an Enhanced Oil Recovery (EOR) element. Such limitations has brought about a newer subjects referred to as LSWI which deals with improving ionic composition of the low salinity brine, a subject to which a lot of attention have been allocated in the recent years.

Combining the two named methods of low salinity and surfactant flooding, a new approach namely Low Salinity Surfactant Flooding (LSSF) is born, which is the center of this study. It seems that simultaneous application of LSWI and surfactant flooding is a better method than applying them solely and separately (He et al., 2015), obviously studying this new method is more complex and demands detailed researches on surfactant ions-injective water interactions. From the other side, rock type, oil type and formation water salinity subjects also require parallel investigations. There are very few studies conducted on low salinity surfactant flooding, but this method has the potential to improve both IFT and Wettability characteristic of the reservoir rock by adjusting surfactant and brine.
properties (Hosseini et al., 2015; Shabib-Asl et al., 2014b). In the other hand knowing the LSWI theory is to help reduce such costs by determine the most attributes to achieve the goals of surfactant flooding.

The reason being in contrast to moderate and high salinity water injection which destablizies the oil film, LSWI reduces the IFT without destablizing it. On the other hand ion optimization will also dedicate to more wettability alteration applying fewer chemicals (Khanamiri et al., 2015).

**Design of experiment (DOE):** DOE method is comprehensive and effective method compared to similar researches in this area discussing different concentration of chemicals as it has the ability to cover continues rang of chemical concentrations.

Applying DOE methods such as Design-Expert application commingled with experiment’s variable alteration ranges facilitate both test-s analysis and interpretation, at the same time reducing side costs, making them a good replacement for conducting costly investigates with the minimum expenses, accelerating outcome resolution. Applying DOE limits the number of laboratory experiments to the sufficient amount of runs to gain enough results to be able to produce the remaining results based on ANOVA analysis and based on the responses gained for that number of runs which are provided manually to the software. DOE methods are based on strong probability and statistic principles, giving the user the option of defining experiment’s variables ranges, while producing the same outcomes for an optimized number of runs as running tests for the involved elements many times, saving both time and expenses.

DOEs are real-life experiment simulators used in process optimization, which is based on ANOVA. This way, both error and costs are reduced, as well as time is saved. ANOVA analysis has the ability of determining the factors which attribute the most or the least to the results, separating the important factors from unimportant ones.

DOE has wide capabilities which can expand its usages as a trustworthy program, so that it is the opinion of the writer that researches can depend on ANOVA analysis for wettability alteration studies provided in DOE software. For instance, in a recent case study (Al-Hashim et al., 2015) applied this method on finding the relationship between the involved ions in wettability alteration, present in the sample of seawater used (Ca$^{2+}$, Mg$^{2+}$, S$_{SO4}^{2-}$ and Cl).

**CONCLUSION**

- In order to optimize the best LSWI, understating the mechanism behind wettability alteration is critical to help optimize the right elements dedicating to it towards increasing the efficiency of LSWI while at the same time a gateway to possible chemical costs while surfactant flooding.
- Stimulation methods such as UTCHEMsoftware together with ANOVA analysis, as new useful tools will help to better understanding of the mechanism behind LSWI.
- Further research in the area of wettability alteration concepts and reasons in both sandstone and carbonate rock cases is suggested.
- Although LSWI mechanism requires more investigations to be fully determined, but some of the most important contributors are MIE, fines migration/mineral dissolution, wettability alteration.
- Modelling COBR interactions is one of the newest subjects of interest for investigations which is being considered recently by researches. Understating such behaviours will indeed help improve our understating of wettability alteration nature, leading to a better perception of its mechanism.

**RECOMMENDATION**

- COBR interactions in different temperatures and different ions existing in different oil types are topics which need further investigations.
- Introducing a global model consisting of detailed COBR interactions is in primary phases of investigation and requires further comprehensive studies.
- It seems that simultaneous application of LSWI and surfactant flooding; LSSF is a more exclusive method than applying them solely and separately.

**REFERENCES**


