SPE-214154-MS

A Look Ahead to the Future of Surfactant Flooding EOR in Carbonate Reservoirs under Harsh Conditions of High Temperature and High Salinity

Imad A. Adel, Anas Mohammed Hassan, Emad W. Al-Shalabi, and Waleed AlAmeri, Khalifa University of Science and Technology, UAE

This paper was prepared for presentation at the Gas & Oil Technology Showcase and Conference held in Dubai, UAE, 13 - 15 March, 2023.

Abstract

Carbonate reservoirs under harsh conditions of high temperature and high salinity (HTHS) have been exploited through primary and secondary recovery methods. This leaves substantial untapped reserves that require the use of enhanced oil recovery (EOR) techniques. Chemical EOR (CEOR) applications, particularly surfactants, in improving recovery under these HTHS conditions are challenging. Developing suitable surfactants that withstand these conditions can improve water imbibition into the low permeability rock matrix, alter the rock wettability, and significantly lower the interfacial tension. The assessment and evaluation of potential surfactants as EOR agents is of great interest and has a strategic role in unlocking further reserves from the vast accumulations of light oil in low permeability carbonates. However, the implementation of surfactants under these conditions faces various challenges, such as stability, compatibility, and high retention values, which need to be overcome for successful applications. This paper provides comparative review analyses and critical discussions on the recent developments to overcome these obstacles and the promising potential for successful surfactant flooding implementations in carbonates.

Surfactant selection is a complicated process, where the surfactant formulation needs to pass several screening techniques. In this paper, limitations, requirements, and aspects affecting the IFT, microemulsion phase behavior, and retention were thoroughly reviewed. Surfactant retention remains the primary factor limiting the implementation of surfactants in carbonate reservoirs under harsh conditions. Nevertheless, recent laboratory studies (screening and corefloods) showed that chemical formulations, including new classes of surfactants with suitable solvents and alkalis, showed excellent performance with minimal retention values under these conditions. Field studies and pilots of surfactant EOR in carbonate reservoirs were also reviewed, highlighting procedures, achievements, challenges, and the way forward to successful applications. A list of recommendations and conclusions is provided at the end of the study based on the literature and our expertise in this area. Surfactant EOR has long been considered impractical in the high temperature and high salinity conditions present in carbonate reservoirs. This study reviews the latest developments and positive outcomes that change this perception and aid in unlocking these reserves. The study is also considered a guide to starting surfactant flooding projects in carbonates under harsh conditions in the Middle East region and elsewhere.

Introduction

Carbonate reservoirs contain most global oil and natural gas reserves, particularly in the Middle East. As these reservoirs are maturing and the ease to produce these reserves through conventional primary and secondary recoveries diminishes, utilizing enhanced oil recovery (EOR) methods becomes indispensable to sustain and prolong production. Nevertheless, enhancing oil recovery in these mature carbonate reservoirs is difficult due to the existing unfavorable conditions such as low permeability, mixed-to-oil wettability nature, high temperature, and high salinity with high levels of divalent ions.

Characteristics of Carbonate Reservoirs.

Carbonate reservoirs are a type of rock formation that contain hydrocarbons, such as oil and natural gas. Several factors can influence the formation and characteristics of carbonate reservoirs. These include the source rock's type and composition, the reservoir's burial history, and structural features such as faults and folds.

The source rock's type and composition can significantly impact the characteristics of carbonate reservoirs. For example, if the source rock is primarily composed of organic-rich shales, the resulting reservoir rock may be high in total organic carbon (TOC) and has a high hydrocarbon generation potential (Shmoker, 1994). On the other hand, if the source rock is composed of limestones, the resulting reservoir rocks may have a lower TOC content but still have a high generation potential due to the high calcium carbonate content (Shmoker, 1994).

The burial history of a carbonate reservoir is important since it determines the degree to which it has been subjected to high levels of heat and pressure. This can influence the quality of the hydrocarbons in the reservoir, as well as the characteristics of the rock itself (Neilson et al., 1996). In addition, structural features such as faults and folds can also influence the formation and characteristics of carbonate reservoirs. These features can create traps for hydrocarbons, rendering the reservoir with a significant amount of hydrocarbons.

One of the main characteristics of carbonate reservoirs is their high temperature. These reservoirs are often found in deep, subsurface environments where temperatures reach up to 300°F (150°C) or higher. The high temperature of carbonate reservoirs can significantly influence the physical and chemical properties of the hydrocarbons they contain. Another characteristic of carbonate reservoirs is their high salinity and high levels of divalent ions (hardness), such as magnesium and calcium ions. The brine's high salt and hardness content can have several impacts on exploration and production activities. For example, it can increase equipment corrosion rendering the extraction of hydrocarbons more difficult.

Carbonate reservoirs are known to have a mixed-to-oil wet wettability nature, meaning that the rock surfaces are partially wetted by oil and water. This wettability is primarily determined by the rock's mineralogy, porosity, and pore structure (Alotaibi *et al.*, 2010). For example, reservoirs containing high amounts of calcite (CaCO3) tend to be more oil-wet, while those with high amounts of dolomite (CaMg(CO3)2) tend to be more water-wet. In addition, the pore size and shape also play a significant role in the wettability of carbonate reservoirs. Smaller, more irregular pores tend to be more oil-wet, while larger, more regular pores tend to be more water-wet (Ahmadi *et al.*, 2018). This wettability nature of carbonate reservoirs can significantly impact the recovery of oil and gas, as it can affect the fluid flow dynamics within the reservoir and the efficiency of recovery methods.

Carbonate reservoirs are also known for their high heterogeneity level, rendering them challenging to study and predict. Heterogeneity can occur at different scales, including within rock types, between layers, and across the entire reservoir. This complexity can affect fluid flow, pressure, and recovery efficiency. Advanced characterization techniques, such as 3D geologic modeling, can aid in better understanding the heterogeneity of carbonate reservoirs and improving recovery efficiency (Hassan *et al*., 2023a and 2023b).

However, the complexity of carbonate reservoirs means that understanding and predicting their behavior is still a major challenge in the industry.

In summary, carbonate reservoirs are an important source of hydrocarbons. However, their high temperature, high salinity and hardness, high heterogeneity, and mixed-to-oil wettability pose unique challenges for exploration and production activities. Therefore, understanding the factors that influence the formation and characteristics of these reservoirs is crucial for successful exploration and production.

EOR in Carbonate Reservoirs.

Enhanced oil recovery (EOR) techniques are increasingly being used to extract oil from more challenging reservoirs, including carbonate reservoirs in harsh environments like these in the Middle East. These reservoirs present several challenges rendering traditional oil recovery methods less effective and requiring advanced EOR techniques to increase oil recovery.

One of the main challenges of recovering oil from carbonate reservoirs is the low permeability of the rock. Carbonate rocks have high porosity, but the pores are often plugged with minerals or other materials that reduce oil flow. This can be especially problematic in reservoirs with oil-wet wettability, as the oil may become trapped in the pores of the rock and difficult to recover (Pal *et al.*, 2018). Therefore, EOR techniques that can increase oil flow through the rock, such as chemical or thermal methods, may be required to overcome this challenge.

Harsh environmental conditions can also render oil recovery more difficult in carbonate reservoirs. For example, offshore platforms may be exposed to rough sea conditions, high winds, and saltwater corrosion leading to damage in equipment and difficulty in operating. Similarly, desert regions may have high temperatures, high salinity, low humidity, and limited access to water, which can affect the performance of EOR techniques that rely on water injection or other fluids (Larson, 2012). To address these challenges, oil companies may need to use specialized equipment and materials or adopt alternative EOR techniques better suited to harsh conditions.

Despite the challenges of enhanced oil recovery in carbonate reservoirs under harsh conditions, EOR techniques can significantly recover the remaining amount of oil (residual oil and/or unswept oil) that can be recovered from these reservoirs. For example, surfactant flooding has been used to increase capillary trapped residual oil through mainly interfacial tension (IFT) reduction. More discussions on surfactant flooding, which is the main scope of this work, are highlighted in the subsequent sections.

Role of Surfactant Flooding in EOR.

Surfactant flooding is a chemical-enhanced oil recovery (CEOR) technique that involves injecting surfactants, or surface-active agents, into an oil reservoir. The purpose of surfactant flooding is to alter the surface tension of the oil-water interface in the reservoir, rendering it easier to extract oil from the rock formations (Adel et al., 2018 and Alvarez and Schechter, 2016). The primary method of recovery is the counter-current imbibition driven by the gradient in capillary pressure, which shifts the capillary pressure from negative to positive, mobilizing oil in counter-current movement (Kathel and Mohanty, 2013). This is accomplished by reducing the interfacial tension between the oil and water phases, which allows the oil to be more easily mobilized and removed from the reservoir.

Surfactant flooding is typically used in conjunction with other EOR techniques, such as polymer flooding. In a typical surfactant flooding process, a surfactant solution is injected into the reservoir, followed by a displacing fluid, such as water or a polymer solution. The surfactant solution reduces the interfacial tension between the oil and water phases, allowing the displacing fluid to easily displace the oil and push it toward the production wells. (Zheng *et al.*, 2019) However, this creates instability in the displacing front; hence, a mobility control agent (polymer) is often used.

There are also several disadvantages of surfactant flooding. One of the main drawbacks is the cost of the surfactant chemicals, which can be expensive. Furthermore, surfactant flooding can be challenging to implement in reservoirs with high temperatures and high salinity, as these conditions can cause the surfactants to degrade or become ineffective.

Despite these challenges, surfactant flooding has proven to be a valuable EOR technique for increasing oil recovery in various reservoirs. However, further research and development are needed to optimize the use of surfactants in EOR and to address the challenges associated with their implementation.

Surfactant EOR in Carbonate Reservoirs

While surfactant EOR has been successfully applied in many oil reservoirs worldwide, it has traditionally been less effective in carbonate reservoirs than in sandstones due to the unique challenges posed by high temperatures, high salinity, and hardness in these reservoirs.

Challenges and Limitations of Surfactant Flooding in Carbonate Reservoirs under Harsh Conditions.

This section describes the challenges and limitations of surfactant flooding in carbonates highlighting surfactant stability, surfactant effectiveness, high carbonate heterogeneity, and surfactant retention aspects.

Surfactant Stability.. One of the main challenges of using surfactant EOR in carbonate reservoirs is the stability of the surfactants at high temperatures and high salinity reservoir fluids. The latter could lead to surfactant degradation and reduced effectiveness. High temperatures can cause thermal degradation of the surfactant, leading to a reduction in the surfactant's ability to reduce interfacial tension. High salinity can also cause ionic degradation of the surfactant, resulting in the formation of insoluble precipitates and a reduction in surfactant performance (Abalkhail, 2018).

Surfactants typically comprise a hydrophobic (water-repellent) portion and a hydrophilic (water-attracting) portion. The stability of a surfactant is largely determined by the balance between these two portions, with a more balanced surfactant being more stable. High temperatures can cause the hydrophobic portion of the surfactant to break down, leading to instability (Saputra *et al.*, 2019). High salinity can also cause instability, as the salt ions can interact with the hydrophobic portion of the surfactant and disrupt the balance between the hydrophobic and hydrophilic portions.

Surfactant Effectiveness.. In addition to stability issues, high temperature and high salinity conditions can also affect the effectiveness of surfactant EOR. High temperatures can cause the surfactant to break down more quickly, reducing its effectiveness. High salinity can also affect the effectiveness of the surfactant, as the salt ions can interfere with the surfactant's ability to reduce the interfacial tension between oil and water (Kamal *et al.*, 2017). Therefore, both high temperature and high salinity conditions can affect the performance of surfactants in enhancing oil recovery (Bashir *et al.*, 2017).

High Carbonate Heterogeneity.. Another challenge facing surfactant EOR in carbonate reservoirs is the high heterogeneity and complexity of these reservoirs. The latter can lead to uneven distribution of the injected surfactant and reduced sweep efficiency. In addition, carbonate reservoirs often have high rock properties and fluid composition variations, which can result in preferential flow and channeling of the injected fluids, leading to poor sweep efficiency (Pal *et al.*, 2018).

Surfactant Retention.. Surfactant retention onto mineral surfaces in carbonate reservoirs is another significant challenge in EOR operations using surfactant-based methods. The retention of surfactants on carbonate rock surfaces has been a well-known issue for a long time (Lu *et al.*, 2014a). It has been suggested that this could be a major obstacle to the economic feasibility of chemical EOR (CEOR) in carbonate reservoirs. In the past, the primary focus of CEOR has been focused on sandstone reservoirs. As a result, the developed surfactant chemical families have mainly been tailored to prevent adsorption on negatively charged silica surfaces rather than positively charged calcite surfaces in carbonates (Levitt *et al.*, 2016).

The main mechanisms for surfactant retention in EOR are adsorption, precipitation, and phase partitioning. Adsorption is the process by which surfactants adhere to the surface of solid particles in the reservoir, such as rock and minerals. Various models, including the Langmuir and Freundlich models, can describe the adsorption of surfactants. According to these models, surfactants' adsorption capacity increases with the surfactant concentration and decreases with the increase in temperature (Maubert *et al.*, 2018). Precipitation refers to the formation of insoluble surfactant compounds in the reservoir. This mechanism occurs when the surfactant concentration exceeds its critical micelle concentration (CMC)). The CMC is the concentration at which surfactant molecules aggregate to form micelles, which are insoluble in oil. Therefore, the precipitation of surfactants can be controlled by adjusting the surfactant concentration and P.H. (Stegemeier *et al.*, 1977). Finally, phase partitioning is the process by which surfactants distribute between the oil and water phases in the reservoir. The partition coefficient of a surfactant is a measure of its ability to partition between oil and water. A surfactant with a high partition coefficient will preferentially partition into the oil phase. In contrast, a surfactant with a low partition coefficient will preferentially partition into the water phase (Graciaa *et al.*, 1987).

Retention of surfactants on mineral surfaces in carbonates is the main obstacle to achieving economic success in enhanced oil recovery (EOR) operations, especially using anionic surfactants.

Addressing the Challenges Posed by Harsh Conditions in Carbonate Reservoirs.

Typically, only a small portion of the oil in known reserves can be extracted using current primary and secondary recovery techniques. Therefore, researchers have long aimed to develop tertiary recovery methods, such as chemical-enhanced oil recovery (CEOR), to improve overall oil recovery (Zhang et al., 2019a, and 2019b). With high oil prices, research in EOR, particularly surfactant processes, has gained significant attention. Conventional surfactants developed in recent years have limitations in harsh environments of HTHS, rendering the development of new and high-performance surfactants crucial. Recently, new types of surfactants have been developed and evaluated for improved oil extraction. These surfactants are necessary for oil field operations under challenging reservoir conditions where it is hard or impossible to find standard surfactants with properties such as very low interfacial tension, stability in water, thermal stability at high temperatures, low retention, and tolerance to high salinity and hardness (Lu et al., 1014b).

In recent years, significant advancements in surfactant flooding technology have addressed these challenges. Researchers have proposed several strategies to overcome the challenges mentioned above and improve the effectiveness of surfactant flooding in carbonate reservoirs. These include, but are not limited to, the use of temperature-stable surfactants, surfactant blends, the optimization of surfactant injection conditions, the development of surfactant formulations that are resistant to ionic degradation, and the use of additives to minimize surfactant retention (Lu *et al.*, 2014a; Levitt *et al.*, 2016; Abalkhail *et al.*, 2020). Additionally, researchers have suggested using smart surfactants, which can adapt to the changing conditions in the reservoir and maintain their effectiveness over a wider range of temperatures and salinities, as well as hybrid smart water/low salinity water applications (Hassan *et al.*, 2022a, 2022b, and 2022c).

One of the main challenges in surfactant flooding in carbonate reservoirs is the high temperature. As previously mentioned, surfactants can degrade at high temperatures, leading to a loss of effectiveness. Researchers have developed surfactants more resistant to thermal degradation to address this issue. In addition to thermal stability, another important factor in surfactant flooding in carbonate reservoirs is the compatibility of the surfactant with the reservoir rock. Unfortunately, carbonate reservoirs often contain minerals that can react with surfactants, causing a loss of effectiveness.

To address the high salinity issue that causes surfactants to destabilize and lose their effectiveness, researchers have developed surfactants that are more resistant to salt. For example, surfactants containing hydroxyethyl moieties had good stability in high salinity conditions and could potentially be used in surfactant flooding in carbonate reservoirs with high salinity. Additionally, a surfactant with at least 30 E.O.

groups and a substantial hydrophobe makes the chemical mixture withstand high levels of divalent ions. (Abalkhaill *et al.*, 2018 and, Ghosh and Mohanty, 2019).

In summary, recent advancements in surfactant flooding technology have the potential to address the challenges of high temperatures and high salinity in carbonate reservoirs. These advancements include the development of surfactants that are more resistant to thermal degradation, more compatible with carbonate minerals, and more resistant to salt and hardness.

Despite these efforts, surfactant flooding remains less effective in carbonate reservoirs than in sandstone reservoirs. Therefore, further research is needed to fully understand the mechanisms that can tackle the challenges discussed, quantify these surfactants' potential, and optimize their use in surfactant flooding for carbonate reservoirs. In general, the HTHS conditions in carbonate reservoirs render it difficult to use surfactant EOR effectively. While some progress has been made in developing more stable and effective surfactants under these conditions, much more research is needed to make surfactant EOR a practical option in carbonate reservoirs.

The need for surfactant EOR in carbonate reservoirs under harsh conditions is driven by the rising need for oil and gas, the depletion of conventional oil reserves, the lack of major huge oil field discoveries, and the need to extract oil from more challenging reservoirs. To meet this need, oil companies must develop and implement advanced EOR techniques to overcome the technical and environmental challenges of recovering oil from carbonate reservoirs.

Below is a description and discussion of the efforts made to address these challenges for carbonates in different design stages, including screening, corefloods, and field applications.

Surfactant Screening

Identifying a surfactant class that can resist both high temperature and high salinity is one of the key challenges in the field of chemical enhanced oil recovery (EOR). This process involves laboratory screening of surfactants by evaluating the phase behavior and cost considering reservoir-specific properties. According to Levitt *et al.* (2009), the surfactant selection process begins with phase behavior testing. Then, it continues to corefloods using combinations of chemicals such as co-surfactants, co-solvents, alkalis, polymers, and electrolytes in the mixture.

It is widely recognized that reducing interfacial tension (IFT) between crude oil and water is critical to mobilize residual oil saturation. Low IFT can be achieved with various surfactants; however, the surfactant selection for a particular reservoir is complicated. It must also meet other stringent requirements, including low retention, compatibility with electrolytes and polymers, thermal and aqueous stability, and low cost (Lu *et al*., 2012). Retention of surfactant can be caused by adsorption onto rock surfaces, but other factors, such as phase trapping, can also play a significant role. Nevertheless, there is a well-established association between the phase behavior of microemulsion and IFT, which can be used to quickly screen surfactant for a given reservoir and predict the most likely surfactant to perform best in more complex and corefloods.

In the surfactant screening stage, surfactants must meet certain criteria. The solubilization parameter must be greater than 10, and the solution must be a low-viscosity microemulsion phase with minimal macroemulsions. The solution must also be clear and transparent at reservoir temperature without crude oil (Levitt *et al.*, 2016). Additionally, adsorption should be below 0.2 mg/g-rock to meet the economic feasibility.

To sum up, selecting a surfactant class that can resist HTHS conditions is a key challenge in the field of chemical-enhanced oil recovery. Recent advancements in surfactant synthesis, molecular structure, and performance relationship have identified promising high-performance surfactants. The surfactant selection process starts with laboratory screening. It progresses to corefloods by considering the reservoir-specific information and evaluating the chemical EOR formulation requirements, such as solubilization parameter, viscosity, transparency, and adsorption (Levitt *et al.*, 2013).

Reduction of Surfactant Retention in Carbonates.

As was previously mentioned, surfactant retention is a crucial aspect in surfactant screening. Minimizing surfactant retention in carbonates under harsh conditions can be achieved through various methods. One approach is to use surfactants specifically designed to be less adsorptive to carbonate rock, such as cationic surfactants, or to use a blend of surfactants with complementary adsorption properties. However, cationic surfactants show poor IFT performance, lack chemical stability under harsh conditions, and are generally more expensive than anionic surfactants.

Another approach is to use chemical treatments, such as the addition of alkali, to alter the surface charge of the carbonate rock and reduce the attraction between the surfactant and the rock. Adding alkali, such as sodium hydroxide (NaOH), can reduce surfactant adsorption in carbonate rock because it can alter the surface charge of the rock. Carbonate rock surface charge is positive due to the presence of carbonate ions. Adding NaOH can neutralize the positive charge and make the surface less attractive to anionic surfactants, leading to less adsorption.

Carbonate reservoirs usually contain significant gypsum and anhydrite, limiting conventional alkalis' use. Using sodium carbonate on rocks containing anhydrite will cause calcium carbonate to form, while using sodium hydroxide on rocks containing dolomite will cause magnesium hydroxide to precipitate. Ammonia alkali is a better option for reservoirs with anhydrite because it can handle high levels of divalent ions (Abalkhail et al., 2020).

Using a combination of co-solvents and different types of surfactants can decrease the thickness of microemulsions and decrease the amount of surfactant retained (Tagavifar *et al.*, 2017). Surfactant retention caused by phase trapping can also be reduced by a negative salinity gradient (Upamali *et al.*, 2018), i.e., the salinity of the polymer drive is lower than the salinity of the surfactant slug. A negative salinity gradient also significantly increases a surfactant flood's robustness in several significant ways (Abalkhai, 2018). Establishing a salinity gradient in a chemical flood is crucial for it to be effective. The gradient should be carefully designed to ensure that the injected surfactant solution has the appropriate salinity, which is lower than the initial brine and higher than the salinity of the polymer drive. Research by Hirasaki et al. (1983) showed that a negative salinity gradient, where the salinity decreases from field brine to polymer drive, can reduce surfactant retention and promote the formation of a type III microemulsion between brine and oil. Additionally, a negative salinity gradient strengthens the resilience of the flood, as reservoir conditions can vary and affect the optimum salinity.

Recently, scholars have been studying the utilization of sacrificial agents to decrease surfactant adsorption. Sacrificial agents are cheap chemicals that can decrease surfactant adsorption by favorably adsorbing onto the rock surface before surfactants do. (Adila *et al.*, 2020). For example, ShamsiJazeyi et al. (2014) conducted a study to examine the impact of using sodium polyacrylate, an inexpensive alternative, on various minerals and rocks in combination with two distinct types of anionic surfactants. They found that using sodium polyacrylate decreased the adsorption of anionic surfactants on minerals such as carbonates and clay.

Advances in Surfactants for HTHS Carbonate Rocks

Recent technological advancements, such as the synthesis of novel surfactant classes, and a greater comprehension of the relationship between surfactant composition and performance, have led to the ability to create high-performing surfactants able to withstand HTHS conditions. This section describes and discusses some of these potential surfactants.

Guerbet Alkoxy Carboxylate (GAC).

A new class of anionic surfactants called Guerbet alkoxy carboxylate (GAC) has been developed and tested for CEOR, showing outstanding performance at HTHS conditions. GAC surfactants provide branched and large hydrophobic groups with the ability to vary the number of alkoxylate groups and remain stable in both basic and non-basic conditions at temperatures up to 120°C or higher (Lu et al., 2012). In addition, the amount of P.O. and E.O. groups in these surfactants can be adjusted and optimized to handle a wide range of oils in various temperatures, salinity, and hardness conditions (Lu et al., 2014a).

GAC + IOS.. Combining a carboxylate surfactant and a sulfonate co-surfactant, such as internal olefin sulfonate (IOS), results in a synergistic interaction that improves the performance and further reduces the total chemical cost (Lu *et al.*, 2014b). With GAC surfactants, it is possible to achieve a clear aqueous solution with low interfacial tension with oils, even in harsh conditions such as high salinity, high hardness, and high temperature (Lu *et al.*, 2012). Combining the Guerbet alkoxy carboxylate surfactant with a sulfonate co-surfactant in a mixture often results in the desired extremely low interfacial tension and stability in high salinity aqueous conditions, while using either surfactant alone is not sufficient (Lu *et al.*, 2014b).

Abalkhail *et al.* (2020) developed an ASP chemical formulation designed for enhanced oil recovery in high permeability, non-fractured, HTHS carbonate reservoir. The formulation was designed to have a low interfacial tension (IFT) and was tested using a series of microemulsion phase behavior experiments and corefloods at 100°C. Three corefloods were conducted on Indiana Limestone core plugs and one on reservoir carbonate core plug. The tests yielded excellent tertiary oil recoveries of 85.2-93.6% and very low surfactant retentions ranging from 0.02 to 0.11 mg/g-rock. The study utilized a chemical composition of 0.5 wt% C28–35PO-65EO- carboxylate, 0.25 wt% C15-18 IOS, and 0.25 wt% C19–28 IOS. In addition, 1 wt% DIPA-10EO and 0.75 wt% NH_3were used as alkalis instead of NaOH due to high levels of dolomite in the reservoir rock.

These carboxylate surfactants were tested in carbonate corefloods with excellent performance at high temperatures and salinities, indicated by a high rate of oil recovery, minimal pressure changes, and minimal surfactant retention (Lu *et al.*, 2014b). The surfactant formulations in all the coreflooding experiments presented in Table 1 consisted of a primary large hydrophobic surfactant (C24-28–xPO-yEO-carboxylate) and two internal olefin sulfonate cosurfactants (C15-18, and C19-28).

Table 1—Summary of coreflood experiments using GAC + IOS

Reference	Core used	Temp	Chemical Slug Salinity (ppm)	Surfactant Blend	Cosolvent / Alkali	Oil Recovery	Retention (mg/g.rock)
Lu et al. (2012)	Reservoir Carbonate	100 °C	57,000	0.5% **GAC** C28–25PO-25EO-carboxylate, 0.5% **IOS** C15-18	- / -	64.9%	0.086
Lu et al. (2014a)	Estaillade Limestone	100 °C	38,000	0.5% **GAC** C28–25PO-45EO-carboxylate, 0.15% **IOS** C15-18	- / -	94.5%	0.34
	Reservoir Carbonate	100 °C	38,000	0.5% **GAC** C28–25PO-45EO-carboxylate, 0.15% **IOS** C15-18	- / -	72.3%	-
	Estaillade Limestone	100 °C	67,000	1.0% **GAC** C28–25PO-55EO-carboxylate, 0.25% **IOS** C15-18, 0.15% **IOS** C19-23	1% **TEGBE** / -	92.0%	0.30
	Silurian Dolomite	78 °C	62,700	0.66% **GAC** C28–25PO-45EO-carboxylate, 0.4% **IOS** C15-18, 0.3% **IOS** C19-23	1% **TEGBE** / -	91.6%	0.16
Parra et al. (2016)	Silurian Dolomite	78 °C	65,000	0.5% **GAC** C28–25PO-45EO-carboxylate, 0.2% **IOS** C15-18, 0.3% IOS C19-28	- / 3% Na2CO3	91.0%	-
	Texas Cream Limestone	78 °C	80,000	0.5% **GAC** C28–25PO-45EO-carboxylate, 0.2% **IOS** C15-18, 0.3% IOS C19-28	- / 3% Na2CO3	80.0%	-
Maubert et al. (2018)	Indiana Limestone	83 °C	58,000	0.5% **GAC** C28–35PO-20EO-carboxylate, 0.25% **IOS** C15-18, 0.25% **IOS** C19-23	1% **IBA**-3EO / 0.3% **NaOH**	97.7% 99.2% 85.6%	0.12 0.15 0.17
	Indiana Limestone	83 °C	93,000	0.5% **GAC** C28–35PO-30EO-carboxylate, 0.4% **IOS** C15-18, 0.1% **IOS** C19-23	1% **IBA**-3EO / 0.5% **NaOH**	84.5%	0.25
Ghosh and Monahty (2019)	Indiana Limestone	80 °C	86,000	0.50% **GAC** C28–45PO-20EO-carboxylate, 0.5% **IOS** C15-18	- / -	86.0%	0.32
	Indiana Limestone	80 °C	79,000	0.5% **GAC** C24–35PO-40EO-carboxylate, 0.25% **IOS** C15-18, 0.15% **IOS** C19-23	0.25% **Phenol**5EO / -	95.2%	0.27
						98.2%	0.29
						93.0%	0.20
	Indiana Limestone	80 °C	70,000	0.35% **GAC** C24–35PO-40EO-carboxylate, 0.175% **IOS** C15-18, 0.175% **IOS** C19-23	0.175% **Phenol**5EO / -	91.4%	0.20
Abalkhail et al. (2020)	Indiana Limestone	100 °C	60,000	0.5% **GAC** C28–35PO-65EO-carboxylate, 0.25% **IOS** C15-18, 0.25% **IOS** C19-28	1% **IBA**-1PO-10EO / 0.75% **NH3**	85.2% 89.5%	0.06 0.02
	Indiana Limestone Reservoir Carbonate	100 °C	60,000	0.5% **GAC** C28–35PO-65EO-carboxylate, 0.25% **IOS** C15-18, 0.25% **IOS** C19-28	1% **DIPA**-10EO / 0.75% **NH3**	91.8% 93.9%	0.11 0.08
Mejia et al. (2021)	Texas Cream Limestone	78 °C	70,000	0.5% **GAC** C28–25PO-45EO-carboxylate, 0.2% **IOS** C15-18, 0.3% **IOS** C19-23	- / 2% **Na2CO3**, 0.5% **NaOH**	50.0%	0.25
			85,000			38.0% 52.0% 37.0% 46.0%	0.12 0.11 0.15 0.21

Surfactant retention using these chemical formulations is also extraordinarily low. For example, Lu *et al.* (2012) conducted a coreflooding experiment on a reservoir carbonate core plug with an initial connate water salinity of 117,000 ppm at 100°C. The injected surfactant formulation comprised of 0.5 wt% GAC (C28–25PO-25EO-carboxylate) and 0.5 wt% IOS (C15-18) in a 57,000 ppm solution with no co-solvents or alkali. The surfactant retention was 0.086 mg/g-rock; the IOS surfactant resulted in 0.044 mg/g of rock, and the carboxylate surfactant resulted in 0.042 mg/g-rock). In another study, Abalkhail *et al.* (2020) reported surfactant retention as 0.083 mg/g-rock in a reservoir carbonate core at 120°C in a chemical slug salinity of 60,000 ppm. The authors also reported surfactant retention values of 0.02, 0.06, and 0.11 mg/g-rock using outcrop Indian Limestone core plugs under the same temperature and salinity conditions. Surfactant retention values from 25 coreflooding experiments using GAC + IOS surfactant formulations on carbonate core plugs at HTHS conditions are reported in Table 1. The results by Lu *et al.* (2012), Maubert *et al.* (2018), Abalkhail *et al.* (2020), and Mejia *et al.* (2021) are very enticing, with retention values below the economic threshold of 0.2 mg/g-rock.

GAC + ABS.. To find a cheaper alternative cosurfactant to IOS, linear alkyl benzene sulfonate (ABS) surfactant was also considered. ABS surfactants are resistant to high temperatures but unsuitable for enhanced oil recovery at high salinities. Cepsa Research Center has developed a formulation that has been shown to meet the requirements of stability and performance at a high temperature of 120°C and seawater (42,700 ppm), typical conditions for Middle East carbonate reservoirs. Combining ABS with an alkyl ethoxy carboxylate enhanced surfactant solubility in seawater salinity of 42,700 ppm (Montes *et al.*, 2018). Blend and salinity scan experiments resulted in a formulation with an ABS/Carboxylate ratio of 40/60. The researchers reported that this formulation forms a microemulsion with ultralow IFT oil/water at seawater salinity. The formulation is robust as it maintains an ultralow IFT at seawater salinity in the range of 0.12% to 1% of total surfactant concentration.

Coreflooding experiments using the ABS/carboxylate blend in low-permeability carbonate reservoir rocks produced an incremental oil recovery of 32% at 120°C when injected in seawater. However, they showed significant surfactant retention, according to Levitt *et al.* (2016) and Jabbar *et al.* (2017). Adding a low molecular weight polymer and mineral oil to the formulation reduced surfactant adsorption and oil phase trapping. Sandpack experiments did not show any adsorption reduction by adding the mineral oil, but adding both polymer and mineral oil reduced adsorption by 34% (Montes *et al.*, 2018). Coreflood experiments showed that adding mineral oil positively affected injectivity, leading to an earlier oil breakthrough and a narrower oil bank; however, no effect was observed on the overall oil recovery.

In summary, the developed formulation is suitable for producing high oil recovery at high temperatures in carbonate reservoirs; however, the surfactant retention remains high and should be further minimized to yield an economic project.

Alkyl Glyceryl Ether Sulfonate (AGES).

Alkyl Glyceryl Ether Sulfonate surfactants have been studied for their potential use in HTHS carbonates. AGES surfactants have been proven to decrease the interfacial tension between oil and water and enhance the effectiveness of displacement in carbonate reservoirs. Also, it has been observed that these surfactants maintain their effectiveness even after being stored for a year at high temperatures of 100°C (Hocine et al., 2018). Additionally, AGES surfactants are less sensitive to salinity changes in the reservoir brine, which can be a problem with other types of surfactants used in EOR. This renders them more stable and reliable for use in high-salinity environments. The conducted studies suggest that under harsh conditions, AGES surfactants can be used for EOR in carbonate reservoirs.

In a study conducted by AlSofi *et al.* (2022), the researchers successfully developed a robust surfactant formulation using binary surfactant mixtures of Alkyl Glyceryl Ether Sulfonate (AGES) and Olefin Sulfonate (O.S.). This formulation was designed for carbonate reservoirs characterized by high salinities and temperatures. A mixture of a slightly hydrophobic AGES and a highly hydrophobic Olefin Sulfonate (O.S.) in both high salinity injection water (59,000 ppm) and low salinity SmartWater (5,900 ppm) showed high performance for the experimented high temperature (100°C) carbonate (AlSofi *et al.*, 2020). Additionally, the developed surfactant formulations were able to form Winsor type III emulsions and achieved ultra-low interfacial tensions from both spinning drop measurements and Huh-based solubilization ratio calculations. Furthermore, after waterflooding, the S.P. formulation recovered up to 63% of the residual oil. The research also found that larger S.P. slug sizes were beneficial for achieving higher incremental oil with fewer throughputs. However, the synergy between the chemical slug and SmartWater was not observed from an incremental oil recovery perspective, as the chemical slugs were specifically designed for high and low-salinity brines.

Cationic + AEC.

Cationic surfactants alone show poor IFT performance and lack chemical stability. However, when formulated together with alkyl ether carboxylates (AEC), stable systems show Windsor Type III phase behavior and IFT measure in the ultra-low region (Herman et al., 2022). The study by Herman et al. (2022) aimed to create a surfactant formula that could be used in HTHS environments. They found that using cationic and anionic surfactants alone did not provide the desired results, but when combined, they created a stable system with ultra-low interfacial tension. The latter research uncovered a robust surfactant formulation consisting of cationic and alkyl ether carboxylate surfactants that work together synergistically (0.61 wt% C16N(CH3)3Cl + 0.39 wt% C16C18—7PO—10EO—CH2CO2Na). This formulation is soluble, chemically stable, and displays Windsor type III phase behavior with ultra-low IFT at a high temperature of 125°C, high salinity of 139,000 ppm, and high divalent cation concentration of 11,800 ppm.

Additional research is required to comprehend how well these formulations work in porous media, specifically how they adsorb to carbonate rocks and how their effectiveness alters over time when exposed to harsh reservoir conditions.

Field Applications

Several Middle East field studies have been conducted to evaluate the effectiveness of surfactant EOR in HTHS carbonates. One example is the ongoing striving chemical EOR program in the highly heterogeneous Sabriyah-Mauddud (SAMA) carbonate formation in Kuwait under harsh conditions of high 78°C and high formation brine salinity of 235,000 ppm. The other example is in a super-giant carbonate field located offshore Abu Dhabi, UAE, with a temperature of 83°C and a formation water salinity of 190,000 ppm. A description of these two field-scale projects is provided below.

Sabriyah-Mauddud (SAMA) Formation, Kuwait.

Carlisle et al. (2014) reported that a series of single-well ASP (Alkaline Surfactant Polymer) pilots were conducted in the SAMA formation. The pilots revealed how the ASP chemicals performed in a highly heterogeneous limestone formation and how to improve the design and interpretation of SWCT (Single Well Chemical Tracer) tests in challenging conditions. There was a significant reduction in Sor from 0.39 to 0.06 during the pilot at Well B Repeat, which is consistent with laboratory coreflood results. The injectivity of highly viscous chemical solutions was excellent, despite the low matrix permeability of the formation in the order of 20 mD. The new chemical formulation, which uses a novel, large-hydrophobe Guerbet alkoxy carboxylate (GAC) surfactant with a mixture of high carbon number IOS co-surfactants (0.65 wt% C28-25PO-45EO-carboxylate, 0.85 wt% IOS), had an optimum salinity of 88,000 ppm corresponding to an ultra-low IFT of 0.001 mN/m at reservoir temperature. This formulation performed well in the SAMA formation's extreme heterogeneity and unfavorable salinity conditions. The results of the SWCT tests, presented in Table 2, provide a strong technical foundation for future multi-well pilot tests.

Table 2—Summary of SAMA pilots (Carlisle *et al.*, 2014)

Reservoir conditions	
Temperature	98 °C
Formation Brine	200,000 ppm
Sea Water	42,000 ppm

Chemical		Concentration
Type	Name	(wt%)
Surfactants	GAC	0.65
	IOS -- C15-18	0.40
	IOS -- C19-28	0.45
Additive	Na4 EDTA (Chelating-agent)	1.00
Co-solvent	IPA -- Isopropyl alcohol	0.23
Polymer	FP 3300	1.00
Alkali	Na2CO3 -- Sodium Carbonate	3.00

Chemical Formulation	
Solubilization ratio	17
Optimum Salinity	93,000 ppm

	Salinity (ppm TDS)			
EOR Slug	Well A	Well B	Well C	Well D
Pre-ASP Water Buffer	118,000	98,000	146,000	142,000
ASP	83,000	86,000	96,000	96,000
Polymer Drive 1	88,000	60,000	66,000	68,000
Polymer Drive 2	52,000	56,000	60,000	48,000
	ASP Test Results Summary			
	Well A	Well B	Well C	Well D
Waterflood Sorw	0.29	0.42	0.33	0.39
Reduction in Sor	65%	55%	45%	85%

Al-Murayri *et al.* (2017) developed an optimized chemical formulation using the same optimized surfactant formulation used by Carlisle *et al.* (2014) but adding co-solvent and other additives to improve the feasibility of previous SWCT tests in the SAMA reservoir. They conducted two SWCT tests in Well A of SAMA to evaluate the effectiveness of ASP in increasing oil recovery. The first test established a residual oil saturation of 0.28, and the second test resulted in a 24% saturation unit reduction with an ASP displacement efficiency of 86%.

Furthermore, Al-Murayri et al. (2022) reported encouraging CEOR field results from the first multi-well ASP pilot project in a carbonate reservoir under harsh conditions worldwide. The use of ASP flooding has yielded promising results with minimal chemical injection. The average oil rate has significantly increased, and the oil cut has grown four-fold after ASP flooding. Data from the field suggests that concerns about in-situ scale risks due to the chemical flood were exaggerated, as scale problems were minimal even without scale inhibition. The ongoing ASP flooding process has provided valuable operational insights and field data to assess the feasibility of implementing phased ASP flooding on a commercial scale.

Abu Dhabi Offshore Field, UAE.

Al-Amrie et al. (2015) reported on the first successful pilot of chemical enhanced oil recovery (EOR) in the United Arab Emirates in an offshore carbonate reservoir with high-temperature (83°C) and high-salinity formation water (190,000 ppm). They conducted extensive research to select surfactants that would be suitable for use in such conditions, ultimately identifying and synthesizing a new class of surfactants that had improved tolerance for high temperatures and salinities compared to commercially available options. They then conducted a single-well pilot to quickly and cost-effectively test their proprietary surfactant and polymer compounds' effectiveness in reducing residual oil saturation under reservoir conditions.

Moreover, Morel *et al.* (2016) reported on the final formulation used in the pilot, which consisted of a 0.4 pore volume slug of 1.35% active surfactant plus 1% clarifier, and a terpolymer in a brine solution simulating a mixture of seawater and local aquifer water. This formulation did not require a preflush, unlike a similar pilot conducted at the same time on the SAMA field in Kuwait. However, the pilot ultimately failed as the surfactant-polymer slug was back-produced. An injection of a surfactant slug dissolved in water was then performed, followed by a chase water injection to push the chemical slug. Despite this, the results of the surfactant flood showed a significant decrease in remaining oil saturation (4%), indicating a relative success of the surfactant pilot.

Jabbar et al. (2017) later examined a chemical mixture's effectiveness in the same HTHS Abu Dhabi offshore carbonate reservoir. They conducted experiments at a temperature of 100°C and formation water salinity of 200,000 ppm. The first mixture (S.P.) included a polymer, a primary surfactant called Guerbet alkoxy carboxylate (GAC) as a primary surfactant, a blend of IOS surfactants, and phenol as a co-solvent. The second mixture (ASP) was the same, with sodium carbonate added to reduce retention. The phase behavior, coreflood injection schemes, and results are summarized in Table 3. The latter table shows that both tests successfully mobilized residual oil, recovering 88% and 82%, respectively, equivalent to 97% and 93.5% of the original oil in the core (OOIC). However, the surfactant retention of 0.99 mg/g-rock and 0.24 mg/g-rock were higher than the economic threshold, indicating that the economics of using surfactant EOR would be difficult, even under ideal conditions with low surfactant retention and sufficient thermal stability. Therefore, future research should address ways of minimizing surfactant retention to meet the economic threshold of 0.2 mg/g-rock.

Table 3—Summary of S.P. and ASP phase behavior and corefloods experiments (Jabbar *et al.*, 2017)

	Phase behavior results			
	SP		ASP	
Solubilization ratio	10		13	
IFT (dynes/cm)	0.003		0.002	
Optimum Salinity (ppm)	63,000		57,000	
Aqueous Stability (ppm)	77,000		83,000	
	SP		ASP	
	Salinity (ppm)	PV injected	Salinity (ppm)	PV injected
Waterflood	70,000	5.00	70,000	5.00
SP/ASP 1	74,000	1.04	66,000	0.69
SP/ASP 2	42,000	0.30	48,000	0.30
Polymer Drive 1	42,000	1.25	48,000	0.68
Polymer Drive 2			48,000	1.91
	Reservoir Core Flood Results			
	SP		ASP	
RF of the residual oil post-waterflood	88%		82%	
Incremental recovery post chemical flood	24.9%		26.3%	
Original oil in core (OOIC) RF	97%		93.5%	
Surfactant Retention (mg/g of rock)	0.99		0.24	

Discussion and Concluding Remarks

The challenges facing surfactant EOR in HTHS carbonate reservoirs are significant. Nevertheless, several potential approaches are used to address these challenges and improve the effectiveness of this technique. These approaches include using specialized surfactants that are more stable and effective under these conditions. By addressing these challenges, it is possible to expand the use of surfactant flooding to carbonate reservoirs under harsh conditions and improve the efficiency of oil recovery in these reservoirs.

Recent technological advancements, such as the synthesis of novel surfactant classes, and a greater comprehension of the relationship between surfactant composition and performance, have led to the ability to create high-performing surfactants able to withstand HTHS conditions. Coreflooding tests have revealed that novel Guerbet alkoxy carboxylate (GAC) surfactants and alkyl glyceryl ether sulfonate (AGES) with internal olefin sulfonate (IOS) co-surfactants exhibit exceptional performance across a range of carbonate reservoir conditions, even at high temperatures up to 120°C. Reported surfactant retention values using these novel surfactant formulations are also very encouraging, with retention values below the economic threshold of 0.2 mg/g-rock.

The chemical compositions utilizing these new surfactants can be tailored to work with a variety of crude oils and across a wide range of salinity, hardness, and temperature conditions by incorporating different co-surfactants and co-solvents to form high-performance microemulsion formulations. Further research could explore the potential of these novel surfactants by testing and studying additional co-surfactants and co-solvents to optimize their synergistic effects.

The research suggests that surfactant EOR can effectively improve oil recovery in HTHS carbonates. However, careful selection of surfactants and optimization of the injection strategy are important for maximizing the effectiveness of the process. Further studies should address other challenges associated with carbonate reservoirs, such as fractures, low levels of permeability, and optimizing the injected chemical slug sizes and salinities. We need to understand better the factors that influence the performance of surfactant EOR in these types of environments and to develop more effective surfactant formulations. In addition, the impact of high temperature and salinity on the surfactant-rock interactions also needs further study. This includes evaluating the effect of these conditions on the adsorption of surfactants on carbonate rock surfaces and minimizing surfactant adsorption to meet the economic limit of the EOR projects.

Surfactant EOR has long been considered impractical in carbonate reservoirs' high temperature and high salinity conditions. However, the results discussed in this paper are amply promising for applying surfactant EOR in HTHS carbonate reservoirs to warrant additional research and development projects funding to aid in unlocking these reserves. In addition, the industry has fully acknowledged the potential impact of recent technological advancements in surfactant EOR and its tremendous potential to become a prominent method in enhanced oil recovery in HTHS carbonates. Hence, additional field studies, such as pilot projects or limited field deployments, are required to confirm laboratory studies' results and gather useful information for implementing surfactant-based EOR methods in HTHS carbonate reservoirs.

Acknowledgments

The authors thank the Petroleum Engineering Department at Khalifa University of Science and Technology (K.U.) for their financial and technical support.

Nomenclature

ABS	Alkyl Benzene Sulfonate
AEC	Alkyl Ether Carboxylates
AGES	Alkyl Glyceryl Ether Sulfonate
ASP	Alkaline Surfactant Polymer
CEOR	Chemical Enhanced Oil Recovery
CMC	Critical Micelle Concentration
DIPA	Diisopropanolamine
EO	Ethylene-Oxide
EOR	Enhanced Oil Recovery
GAC	Guerbet Alkoxy Carboxylate
HTHS	High-Temperature High-Salinity
IBA	Isobutyl Alcohol
IFT	Interfacial Tension
IOS	Internal Olefin Sulfonate
O.S.	Olefin Sulfonate
PO	Propylene-Oxide
RF	Recovery Factor
SAMA	Sabriyah-Mauddud
SBA	Surfactant Bridging Adsorption
SMI	Surfactant Mineral Interactions
S.P.	Surfactant Polymer
SWCT	Single Well Chemical Tracer
TEGBE	Triethylene Glycol Mono Butyl Ether
TOC	Total Organic Content

References

Abalkhail, N., 2018. Chemical Enhanced Oil Recovery Application in a High-Temperature, High-Salinity Carbonate Reservoir. MSc Thesis, The University of Texas at Austin, USA.

Abalkhail, N. A., Liyanage, P. J., Upamali, K. A. N., Pope, G. A., and Mohanty, K. K., 2020. Alkaline-Surfactant-Polymer Formulation Development for a HTHS Carbonate Reservoir. *J. Petrol. Sci & Eng.*, **191**, 107236.

Adel, I.A., Tovar, F.D., Zhang, F. et al 2018. The Impact of MMP on Recovery Factor During CO2 – EOR in Unconventional Liquid Reservoirs. Presented at the SPE Annual Technical Conference and Exhibition, Dallas, Texas, USA. 17. SPE-191752-MS. https://doi.org/10.2118/191752-MS.

Adila, A. S., Al-Shalabi, E. W., and AlAmeri, W., 2020. Recent Developments in Surfactant Flooding for Carbonate Reservoirs Under Harsh Conditions. Paper presented at the Offshore Technology Conference Asia, Kuala Lumpur, Malaysia, 2–6 November. OTC-30318-MS. https://doi.org/10.4043/30318-MS.

Ahmadi, A. and Moosavi, M., Investigation of the Effects of Low-Salinity Waterflooding for Improved Oil Recovery in Carbonate Reservoir Cores. *Energy Sources, Part A: Recovery, Utilization, and Environmental Effects.* **40** (9): 1035–1043, 2018. https://doi.org/10.1080/15567036.2018.1468514

Al-Amrie, O., Peltier, S., Pearce, A., Al-Yafei, A., Morel, D., Bourrel, M., Bursaux, R., Cordelier, P., Jouenne, S., Juilla, H., Klimenko, A., Levitt, D., and Nguyen, M., 2015. The First Successful Chemical EOR Pilot in the UAE: One Spot Pilot in High Temperature, High Salinity Carbonate Reservoir. Presented at the SPE Abu Dhabi International Petroleum Exhibition and Conference, Abu Dhabi, UAE, 9-12 November. SPE-177514-MS. http://dx.doi.org/10.2118/177514-MS.

Al-Murayri, M. T., Hayat, L., Al-Qattan, A., Al-Kharji, A., Bouillot, J., Omonte, G., Salehi, N., and Zaitoun, A., 2022. Deep Reservoir Conformance Control for the Wara Formation of the Greater Burgan Field: Lab Evaluation, Numerical Simulation and Field Implementation Design. Presented at the ADIPEC Conference, Abu Dhabi, UAE. SPE-211430-MS. https://doi.org/10.2118/211430-MS.

Al-Murayri, M. T., Kamal, D. S., Suniga, P., Fortenberry, R., Britton, C., Pope, G. A., Liyanage, P. J., Jang, S. H., and Upamali, K. A. N., 2017. Improving ASP Performance in Carbonate Reservoir Rocks Using Hybrid-Alkali. Presented at the Annual Technical Conference and Exhibition, San Antonio, Texas, 09-11 October. SPE-187213-MS. http://dx.doi.org/10.2118/187213-MS.

Alotaibi, M.B., Azmy, R., and Nasr-El-Din, H.A. Wettability Challenges in Carbonate Reservoirs. SPE Improved Oil Recovery Symposium, 24-28 April, Tulsa, Oklahoma, USA, 2010. SPE-129972-MS. https://doi.org/10.2118/129972-M.S.

AlSofi, A. M., Wang, J., Salaun, M., Rousseau, D., Morvan, M., and Ayirala, S., 2022. SmartWater Synergy with Chemical EOR: Studying the Potential Synergy with Surfactants. Paper presented at the ADIPEC Conference, Abu Dhabi, UAE. SPE-200502-MS. http://dx.doi.org/10.2118/200502-MS.

Alvarez, J. O. and Schechter, D. S., 2016. Altering Wettability in Bakken Shale by Surfactant Additives and Potential of Improving Oil Recovery During Injection of Completion Fluids. Presented at SPE Improved Oil Recovery Conference, Tulsa, Oklahoma, 11–13 April. SPE-179688-MS. https://doi.org/10.2118/179688-MS.

Bashir, A., Haddad, A. S., NS, and Rafati, R. 2021. A review of fluid displacement mechanisms in surfactant-based chemical enhanced oil recovery processes: Analyses of key influencing factors. *Petroleum Science*, **19** (3), 1211–1235. https://doi.org/10.1016/j.petsci.2021.11.021

Carlisle, C., Al-Maraghi, E., Al-Saad, B., Britton, C., Fortenberry, R., and Pope, G., 2014. One-Spot Pilot Results in the Sabriyah-Mauddud Carbonate Formation in Kuwait Using a Novel Surfactant Formulation. Presented at the SPE Middle East Oil & Gas Show and Conference, Manama, Bahrain, 8–11 March. SPE-169153-MS. http://dx.doi.org/10.2118/169153-MS.

Graciaa, A.; Lachaise, J.; Bourrel, M.; Osborne-Lee, I.; Schechter, R.S. and W.H. Wade. 1987. Partitioning of Nonionic and Anionic Surfactant Mixtures Between Oil/Microemulsion/Water Phases. SPE 13030-PA. *SPE Reservoir Engineering Journal*, August 1987

Ghosh, P. and Mohanty, K. K., 2019. Study of Surfactant–Polymer Flooding in High-Temperature and High-Salinity Carbonate Rocks. *Energy and Fuels*, **33** (5): 4130–4145 https://doi.org/10.1021/acs.energyfuels.9b00407.

Hassan, A. M., Ayoub, M., Eissa, M., Al-Shalabi, E. W., Al-Mansour, A., and Al-Quraishi, A., 2022a. Increasing Reservoir Recovery Efficiency through Laboratory-Proven Hybrid Smart Water-Assisted Foam (SWAF) Flooding in Carbonate Reservoirs. *Energies*, **15** (9), 3058.

Hassan, A. M., Ayoub, M., Eissa, M., Al-Shalabi, E. W., Al-Mansour, A., and Al-Quraishi, A., 2022b. Foamability and Foam Stability Screening for Smart Water Assisted Foam Flooding: A New Hybrid EOR Method. Paper presented at the In International Petroleum Technology Conference, Riyadh, S.A. IPTC-22475-MS. http://dx.doi.org/10.2523/IPTC-22475-MS.

Hassan, A. M., Ayoub, M. A., Mohyaldinn, M. E., and Al-Shalabi, E. W., 2022c. Insights into Hybrid Smart Water Assisted Foam (SWAF) Flooding in Carbonate Reservoirs: A Combined Numerical and Experimental Approach. Paper presented at the ADIPEC Conference, Abu Dhabi, UAE. SPE-211439-MS. http://dx.doi.org/10.2118/211439-M.S.

Hassan, A. M., Tachie-Otoo, B. N., Ayoub, M. A., Mohyaldinn, M. E., Al-Shalabi, E. W., and Adel, I. A., 2023a. Numerical Investigation of Hybrid Smart Water and Foam Injections in Carbonate Reservoirs. Presented at the SPE Reservoir Characterization and Simulation Conference and Exhibition, Abu Dhabi, UAE. SPE-212663-MS. http://dx.doi.org/10.2118/212663-MS.

Hassan, A. M., Al-Shalabi, E. W., Ghosh, B., Tachie-Otoo, B. N., Ayoub, M. A., and Adel, I. A., 2023b. Numerical Investigation of Hybrid Carbonated Smart Water Injection (CSWI) in Carbonate Reservoirs. Presented at the Gas & Oil Technology Showcase and Conference, Dubai, UAE. SPE-214163-MS. http://dx.doi.org/10.2118/214163-MS.

Hassan, A.M., Al-Shalabi, E. W., Alameri, W., Kamal, M. S., Patil, S., and Hussain, S. M. S. Ayoub, M., Eissa, M., Bruining, H., and Zitha, P., 2023c. Manifestations of surfactant-polymer flooding for successful field applications in carbonates under harsh conditions: A comprehensive review. *Journal of Petroleum Science and Engineering*,p.111243.

Herman, G., Lichterfeld-Weber, N., and Bittner, C., 2022. Unique Synergistic Surfactant Mixture to Match Ultralow Interfacial Tension with Solubility at High Temperature and High Salinity. Presented at the ADIPEC Conference, Abu Dhabi, UAE. SPE-211475-MS. https://doi.org/10.2118/211475-MS.

Hirasaki, G.J., van Domselaar, H.R., Nelson, R.C., 1983. Evaluation of the Salinity Gradient Concept in Surfactant Flooding. Society of Petroleum Engineers. https://doi.org/10.2118/8825-PA.

Hocine, S., Pousset, B., Courtaud, T., and Degré, G., 2018. Long Term Thermal Stability of Chemical EOR Surfactants. Presented at the SPE EOR Conference at Oil and Gas West Asia, Muscat, Oman, 26-28 March. SPE-190361-MS. https://doi.org/10.2118/190361-MS.

Jabbar, M. Y., Al Sowaidi, A., Al Obeidli, A., Willingham, T. W., Britton, C., Adkins, S., Delshad, M., Xiao, R., and Teletzke, G. F., 2017. Chemical Formulation Design in High Salinity, High Temperature Carbonate Reservoir for a Super Giant Offshore Field in Middle East. Paper presented at the Abu Dhabi International Petroleum Exhibition and Conference, Abu Dhabi, UAE, 13–16 November. SPE-188604-MS. https://doi.org/10.2118/188604-MS.

Kamal, M. S., Hussein, I., and Sultan, A. 2017. Review on Surfactant Flooding: Phase Behavior, Retention, IFT, and Field Applications. *Energy Fuels*, **31**, 7701–7720.

Kahel, P., Mohanty, K.K. 2013. EOR in Tight Oil Reservoirs through Wettability Alteration. Paper SPE 166281-MS, presented at the SPE Annual Technical Conference and Exhibition, New Orleans, Louisiana, USA, 30 September-2 October. SPE-188604-MS. http://dx.doi.org/10.2118/SPE-188604-MS-MS

Larson, A., and Leitko, S. 2020. Recognition and Management of the Distinctions of Harsh Environment FPSO Project Design and Management. Paper presented at the OTC Arctic Technology Conference, Houston, Texas, USA, December 2012 OTC-23831-MS. https://doi.org/10.4043/23831-MS.

Levitt, D., Klimenko, A., Jouenne, S., Boupat, N. P., Cordelier, P., Morel, D., and Bourrel, M., 2016. Designing and Injecting a Chemical Formulation for a Successful Offshore Chemical EOR Pilot in a High-Temperature, High-Salinity, Low-Permeability Carbonate Field. Paper presented at the SPE Improved Oil Recovery Conference, Tulsa, Oklahoma, USA, 11–13 April. SPE-179679-MS. https://doi.org/10.2118/179679-MS.

Levitt, D., Klimenko, A., Jouenne, S., Chamerois, M., and Bourrel, M., 2013. Overcoming Design Challenges of Chemical EOR in High Temperature, High Salinity Carbonates. Presented at the SPE Middle East Oil and Gas Show and Conference, Manama, Bahrain, 10-13 March. SPE-164241-MS. http://dx.doi.org/10.2118/164241-MS.

Levitt, D.B., Jackson, A.C., Heinson, C., Britton, L.N., Malik, T., Dwarakanath, V., and Pope, G.A. 2009. Identification and Evaluation of High-Performance EOR Surfactants. *SPE Res Eng*., **12** (2): 243–253. SPE 100089-PA. https://doi.org/10.2118/100089-PA.

Lu, J., Goudarzi, A., Chen, P., Kim, D. H., Britton, C., Delshad, M., Mohanty, K. K., Weerasooriya, U. P., and Pope, G. A., 2012. Surfactant Enhanced Oil Recovery from Naturally Fractured Reservoirs. Presented at the SPE Annual Technical Conference and Exhibition, San Antonio, Texas, 8-10 October. SPE-159979-MS. https://doi.org/10.2118/159979-MS.

Lu, J., Britton, C., Solairaj, S., Liyanage, P. J., Kim, D. H., Adkins, S., Arachchilage, G. W., Weerasooriya, U., and Pope, G. A., 2014a. Novel Large-Hydrophobe Alkoxy Carboxylate Surfactants for Enhanced Oil Recovery. *SPE J.*, **19** (6): 1024–1034 SPE-154261-PA. https://doi.org/10.2118/154261-PA.

Lu, J., Liyanage, P. J., Solairaj, S., Adkins, S., Pinnawala Arachchilage, G., Kim, D. H., Britton, C., Weerasooriya, U., and Pope, G. A., 2014b. New surfactant developments for chemical enhanced oil recovery. *J. Petrol. Sci. Eng.*, **120**, 94–101 https://doi.org/10.1016/j.petrol.2014.05.021.

Maubert, M., Jith Liyanage, P., Pope, G. A., Upamali, N., Chang, L., Ren, G., and Morel, D., 2018. ASP Experiments in Indiana Limestone using NaOH to Reduce Surfactant Retention. Presented at SPE IOR Symposium, Tulsa, OK, USA. SPE-190187-MS. http://dx.doi.org/10.2118/190187-MS.

Mejía, M., Parra, J. E., Mejía, L. et al 2021a. Experiments and Numerical Simulations of Chemical Enhanced Oil Recovery in Fractured Carbonate Rocks. *J Pet Sci Eng* **199**: 108280. https://doi.org/10.1016/j.petrol.2020.108280.

Montes, J., Blin, N., Alvarez, A. E., Barrio, I., Panadero, A., Rodriguez, R., Coca, M., and Trujillo, F., 2018. Novel Anionic Surfactant Formulation for High Temperature Carbonate Reservoirs. Paper presented at the SPE EOR Conference at Oil and Gas West Asia, Muscat, Oman, 26–28 March. SPE-190353-MS. https://doi.org/10.2118/190353-MS.

Morel, D., Al-Amrie, O., Delattre, E., Cordelier, P., Greder, H., Rivero, M., Remoero, C., Bursaux, R., Peltier, S., and Levitt, D., 2016. Specific Procedure for an Offshore Chemical EOR One Spot Pilot in a High Salinity High Temperature Environment. Presented at the SPE Annual Technical Conference and Exhibition, Dubai, UAE, 26-28 September. SPE-181643-MS. http://dx.doi.org/10.2118/181643-MS.

Neilson, J.E., Oxtoby, N.H., and Simmons, M.D. (1996) Effect of Petroleum Emplacement on Reservoir Quality in the Thamama Reservoirs of Abu Dhabi. SPE-36241, pp. 989–1001.

Pal, S., Mushtaq, M., Banat, F., and Al Sumaiti, A. M., 2018. Review of surfactant-assisted chemical enhanced oil recovery for carbonate reservoirs: challenges and future perspectives. *Petroleum Science*, **15**: 77–102.

Parra, J. E., Pope, G. A., Mejia, M., and Balhoff. M.T., et al 2016. New Approach for Using Surfactants to Enhance Oil Recovery from Naturally Fractured Oil-Wet Carbonate Reservoirs. Paper presented at the SPE Annual Technical Conference and Exhibition, Dubai, UAE, 26–28 September. SPE-181713-MS. https://doi.org/10.2118/181713-MS.

Saputra, I. W. R., Park, K. H., Zhang, F., and Adel, I. A. 2019. Surfactant-Assisted Spontaneous Imbibition to Improve Oil Recovery on the Eagle Ford and Wolfcamp Shale Oil Reservoir: Laboratory to Field Analysis. *Energy Fuels* **33** (8): 6904–6920 https://doi.org/10.1021/acs.energyfuels.9b00183.

Schmoker, J.W. 2005. U.S. Geological Survey Assessment Concepts for Continuous Petroleum Accumulations. U.S. Geological Survey Digital Data Series DDS-69-D: chapter 13, P.P. 1–7.

ShamsiJazeyi, H., Verduzco, R., and Hirasaki, G. J., 2014. Reducing adsorption of anionic surfactant for enhanced oil recovery: Part I. Competitive adsorption mechanism Colloids Surf. *Physicochem. Eng. Asp.*, **453**: 162–167.

Stegemeier, G. (1977). Improved Oil Recovery by Surfactant and Polymer Flooding. New York, NY: Academic Press.

Tagavifar, M., Herath, S., Weerasooriya, U. P., Sepehrnoori, K., and Pope, G. A., 2017. Measurement of microemulsion viscosity and its implications for chemical enhanced oil recovery. *SPE J.*, **23** (1): 66–83 SPE-179672-PA.

Upamali, K. A., Liyanage, P. J., Jang, S. H., Shook, E., Weerasooriya, U. P., and Pope, G. A., 2018. New Surfactants and Co-solvents Increase Oil Recovery and Reduce Cost. *SPE J.*, **23** (6): 2202–2217 SPE-179702-PA. https://doi.org/10.2118/179702-PA.

Zhang, F., Saputra, I.W.R., Adel, I.A., and Schechter. D.S. 2019a. Numerical Investigation of EOR Applications in Unconventional Liquid Reservoirs through Surfactant-Assisted Spontaneous Imbibition (Sasi) and Gas Injection Following Primary Depletion. Presented at the SPE Annual Technical Conference and Exhibition, Calgary, Albert, Canada. SPE-196055-MS. https://doi.org/10.2118/196055-MS.

Zhang, F., Adel, I. A., Saputra, I. W. R. et al 2019b. Numerical Investigation to Understand the Mechanisms of CO2 EOR in Unconventional Liquid Reservoirs. Paper presented at the SPE Annual Technical Conference and Exhibition, Calgary, Alberta, Canada. SPE-196019-MS. https://doi.org/10.2118/196019-MS.