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Full Length Article

Descriptive statistical analysis of experimental data for wettability alteration with surfactants in carbonate reservoirs

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A R T I C L E I N F O

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A B S T R A C T

Surfactants have been the widely used agents to alter the wettability of carbonate rocks to more water-wet and enhanced oil recovery (EOR). As one of major EOR methods, an effective surfactant huff-puff application design requires comprehensive guidelines about where, how, and when this method could be applied. In order to construct such guidelines, a dataset including 338 effective surfactant imbibition tests is established by collecting information from nearly 50 publications. Based on this dataset, descriptive statistical analysis methods are used to conduct data analysis, including three main parts. The first part establishes the application guidelines for surfactant huff-puff treatments which displays suitable application ranges of critical parameters regarding rock, oil, and water. Results show that surfactants can be effectively applied in wide ranges: porosity from 3.1 to 51.7%, permeability from 0.04 to 1458 mD, starting oil saturation from 37.7 to 100%, temperature from 20 to 100 °C, average contact angle from 55 to 180°, oil gravity from 22 to 75.2 °API, oil viscosity from 0.3 to 23 cp, acid number from 0 to 4.5 mg KOH/g oil, base number from 0 to 1.83 mg KOH/g oil, asphaltene concentration from 0 to 10.7 wt%, salinity of connate water and imbibition water from 0 to 263.7 g/l, divalent cations concentration of connate water and imbibition water from 0 to 24.6 g/l. The second part discusses several aspects about design of surfactant huff-puff treatments. Results show that anionic, cationic, and nonionic surfactants have been applied in 83% of tests. Among them is cationic surfactants which have the most frequency. Surfactant concentration is suggested to be remained close or above a critical concentration to obtain the best performance. It is shown that 97% of tests are conducted with surfactant concentration less than 2.0 wt%. In addition, blends of different surfactants and usage of additives could enhance the effectiveness of surfactants. The last part evaluates the performance of surfactant imbibition tests. Results show that surfactants are capable to improve oil recovery either from secondary phase or tertiary phase. In general, the range of oil recovery from secondary phase and tertiary phase are similar, which covers from 1.0 to 93%. However, the average oil recovery from secondary phase is 39.1% which is higher than 32.2% from tertiary phase. Based on this, it is recommended that the treatment timing should be considered in the design of treatments.

1. Introduction

It has been documented that at least 80% of carbonate reservoirs are characterized as oil-wet to neutral-wet [1–4]. Besides, carbonate reservoirs often tend to be naturally fractured. In this way, waterflooding is not regarded as being efficient in carbonate reservoirs. The injected water is not likely to be imbibed into rock matrix to displace oil because of low or negative capillary forces. The injected water tends to follow fractures and bypass rock matrix, which gives rise to early breakthrough and low sweep efficiency. As a result, around 80% of original oil in place (OOIP) is not recovered [5].

Addition of proper surfactants to water is capable to alter the wettability of carbonate rocks from oil-wet towards more water-wet. The ultimate oil recovery can be substantially improved as illustrated by an extensive work. In 1957, a U.S. patent was proposed by Graham et al. [6], where the imbibition process of water in sandstones was enhanced with usage of surfactants. A later U.S. patent was reported in 1988 by Craig [7], in which surfactants were illustrated to promote imbibition recovery process via wettability alteration in oil-wet carbonate rocks from West Texas. A successful surfactant huff-puff treatment in a production well located in West Texas field was included in this patent. This treatment was found to increase oil production by 650

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barrels within five days. Few years later, an extensive work has been reported in the subject of wettability alteration with surfactants in carbonate reservoirs. Information of several field applications are available in literature: Yates field in Texas, USA [8], Cottonwood Creek field in Wyoming, USA [9], Mauddud reservoirs in Bahrain [10], Semoga field in Indonesia [11], Akanskoe field in Tatarstan [12], northern field of Oman [13], and a Chinese oilfield [14]. As indicated in Fig. 1, a typical surfactant huff-puff treatment includes three stages: the injection stage (huff), the soaking stage, and the production stage (puff). Surfactant solutions are injected into the target formation through the well in the injection stage. In the soaking stage, the well is shut-off for a certain period to allow a complete reaction between surfactant solutions and hydrocarbon. During the soaking period, surfactant molecules diffusion occurs, and surfactant molecules interact with active materials adsorbed on carbonate rocks surface. As a result, the wettability of carbonate rocks is altered to more water-wet. The suggested interactions and wettability alteration mechanisms have been summarized in our recently published review paper [15]. The imbibition of water is promoted and much more oil is produced from matrix to highly permeable factures. The well is then returned to open in the production stage. Due to the driving force generated by the pressure drop, the oil is produced with water from a further location of the reservoir to the wellbore.

At the same time of aforementioned field cases, a great deal of laboratory work has been performed on the spontaneous imbibition tests. Up to now, laboratory work is still being reported in literature. Imbibition tests are easily performed and helpful to enhance understanding of wettability alteration via surfactants. Also, imbibition tests data can reflect the recent developments of wettability alteration with surfactants. Apart from that, they are economic tools to evaluate the effectiveness of surfactant huff-puff treatments before implementation in field scales. Based on laboratory results, the oil recovery behavior, and the influence of important factors in target carbonate reservoirs can be investigated using suitable upscaling models [16]. So far, multiple types of surfactant systems have been proved effective to alter wettability in laboratory study, including cationic, anionic, nonionic, zwitterionic (or amphoteric), gemini, and combination of them. The interactions between surfactant molecules and carbonate rocks surface, as well as underlying wettability alteration mechanisms of aforementioned surfactant systems have been reviewed in our recently published paper [15]. However, surfactant huff-puff treatments are not always effective. It is observed that the oil recovery from some treated wells and treated cores is not increased. Therefore, it is essential to explore applicable conditions of surfactant huff-puff treatments.

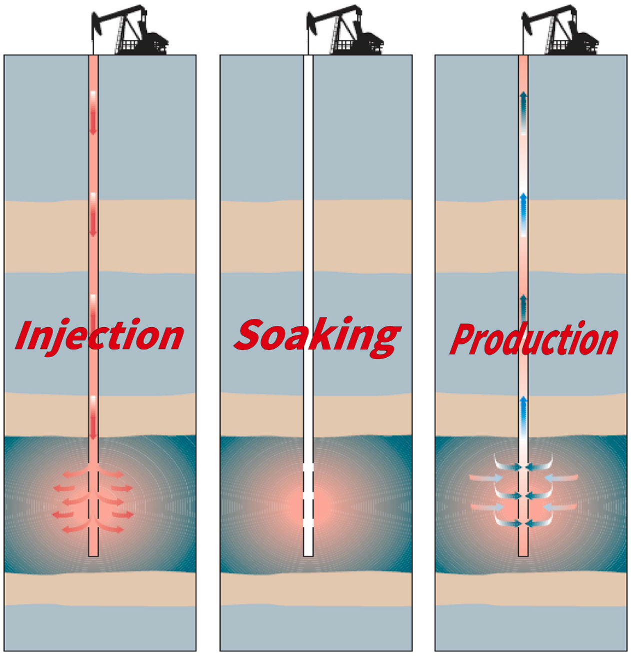

Fig. 1. Schematic of surfactant huff-puff process, modified after Rilian et al. [11].

Screening guidelines or criteria is an appealing form to illustrate specific conditions where a certain EOR method could be implemented effectively. The conditions include both reservoir characteristics and fluid (oil and water) properties [17–19]. Screening guidelines serve as the first term to assist in petroleum engineers screening a feasible EOR method for a given candidate reservoir [17,20–22], which is crucial to the starting of an EOR project. Most commonly, they are developed on a combination of effective applications of EOR methods and expert knowledge. The information of effective applications can be from successful field cases and experimental results. Screening guidelines can be presented in tabular or/ and graphical form [17,19,23]. In the tabular form, the applicable range obtained from statistical analysis of effective applications data for each important parameter is given. In the last four decades, several screening guidelines have been reported and updated by different investigators for surfactant EOR. The information is summarized in Table 1. However, it is to note that current guidelines are mainly established for sandstone reservoirs, where the main function of surfactants is to lower the oil/water interfacial tension (IFT). Application guidelines for surfactant treatments in carbonate reservoirs are rarely found. Weiss and Xie explored the importance of permeability and surfactant concentration in surfactant huff-puff treatments with imbibition tests data [24]. It was shown that both imbibition rate and incremental oil recovery were higher from cores with higher permeability. In addition, no more oil was recovered from cores with permeability less than 1 mD. In view of this fact, 1 mD was determined as the lower limit for effective surfactant huff-puff treatments. Besides that, the surfactant loss resulted from adsorption on large mineral surface was regarded as one possible factor for the failure of surfactant huff-puff treatments. Hence, surfactant concentration needs to be remained above a limit to ensure enough surfactant molecules are active in altering wettability.

In fact, an extensive surfactant imbibition tests have been implemented effectively in global fields. A large amount of data is available in literature, which makes it feasible to construct guidelines. The purpose of this study is to provide comprehensive guidelines for wettability alteration with surfactants in carbonate rocks. The structure of this paper is as follows. Section 2 introduces the process of high-quality dataset construction and general dataset information. Section 3 illustrates descriptive statistical analysis methods applied in this work. Following Section 4 gives application guidelines where wettability alteration via surfactants can be effectively implemented. In addition, design considerations and performance evaluation of effective imbibition tests are discussed in Sections 5 and 6, respectively. Lastly, conclusions are summarized in Section 7.

2. Dataset construction and description

2.1. Data collection and pre-processing

Data of wettability alteration with surfactants are stored in different publications with various formats. This fact makes it a challenging task to create a comprehensive dataset to include information from global projects related with this topic. Dataset in this study is composed of wettability alteration information published from 1996 to 2020 in several data sources, namely published technical papers, project reports, book chapters, and student theses [5,16,24,31–72]. In total, information of 402 surfactant imbibition tests from nearly 50 publications are collected in the dataset. 338 imbibition tests are considered effective, where oil recovery is always improved by means of surfactants. Because the objective of this study is to provide instructive guidelines for wettability alteration with surfactants, only effective imbibition tests are considered in data analysis stages. Possible reasons for ineffective

Table 1
Previous guidelines for surfactant EOR.

EOR methods	Formation types	Oil saturation % PV	Porosity %	Average permeability mD	Temp °C	Depth ft	Net thickness ft	Gravity °API	Viscosity cp	Oil compositions	Salinity g/l	Divalent cations g/l	References
Surfactant/polymer flooding	Sandstone preferred	>30		>20	<79.4	<8000	>10	>25	<30	Light to intermediates (desirable)	<20	<0.5	Taber and Martin. [17]
Surfactant flooding	Sandstone			>40	<93.3				<40		<100		Bailey and Curtis. [25]
Surfactant/polymer flooding	Sandstone preferred	>30	≥20	>40	<93.3	<9000	N.C.	>25	<40	Light to intermediates (preferred)	<100		Goodlett et al. [26]
Micellar/polymer flooding	Sandstone preferred	>35		>10	<93.3	<9000	N.C.	>20	<35	Light to intermediates	<20	<0.5	Taber et al. [27]
Surfactant/polymer flooding		>35		>50	<70				<150		<50	<1.0	Al-Bahar. [28]
Alkaline/surfactant/polymer flooding	Sandstone	43.5–53, Avg. 49	14–16.8, Avg. 15.6	50–60, Avg.56.7	50–68.3, Avg. 52.4	5300–6250, Avg. 3406	N.C.	22–29, Avg. 31.8	15.6–2.63, Avg. 7.1				AI Adasani and Bai. [29]
Surfactant flooding	Sandstone	>30,Med. 40		>10,Med. 152	<93.3, Med. 25.6	N.C.,Med. 1808		N.C.,Med. 36.5	<35,Med. 5.8		<50, Med. 39	<0.1	Sheng. [30]
Surfactant flooding	Sandstone		20	475	35	5740		44.3	5				Zhang et al. [20]

Note:
N.C. is not critical.
Avg. and Med. are average and median value for surveyed projects.

imbibition tests are discussed in the section of performance evaluations. The constructed dataset consists of five categories, including rock properties, fluid properties, surfactant properties, operational conditions, and performance evaluations indicators. The research targets vary in different reports, which gives rise to incomplete information for above-mentioned parameters. As a result, the frequency varies among various parameters in data analysis stages. Apart from missing data, integrating data from varied data sources could result in ununiform data and duplicate data. Analysis results from dataset which is not carefully screened for such problems could be misleading. Following criteria are applied to ensure high quality of dataset.

The ununiform data problem is ascribed to that an identical parameter can be presented in different manners and different units. Some parameters especially for permeability and contact angle are often given in a range rather than a precise figure. To eliminate this problem, a mean value is computed in data analysis. On the other hand, minima of several parameters could be provided in literature. This situation is common for pH of anionic surfactant solutions and aging time interval required for restoring rock to oil-wet state. The pH of anionic surfactant solutions is commonly kept above zero point of charge (ZPC) of carbonate rocks to reduce surfactant adsorption [16,40,45,52]. For these parameters, a minimal value is utilized in subsequent data analysis. Aside from different manners, units of parameters could be various in different data sources. For example, temperature is presented as either °F or °C, salinity is given in part per million (ppm), wt. % or g/l, etc. In this case, each parameter in this dataset is formatted with one defined unit.

Duplicate data arises in the process of establishing application guidelines. Guidelines are formed on important parameters of rock and fluid, and these parameters are often kept constant in surfactant imbibition tests. While other parameters could be changed for various research targets, including surfactant properties, the ratio between surrounding solution volume and rock volume, and performance indicators. For example, given same parameters of rock and fluid, the surfactant concentration is varied to study the impact of surfactant concentration on wettability alteration. As a result, the same rock and fluid parameters are included in the dataset several times, which causes duplicate data problem. If we do not remove the duplicate data, the established guidelines can be biased towards the rock and fluid conditions with more frequency. To eliminate this issue, the policy "one rock/fluid condition, one sample" is utilized to clean duplicate data, where only one sample is chosen to construct guidelines with same rock and fluid properties. Consequently, 290 samples are remained in the stage of establishing application guidelines.

2.2. Worldwide data distribution

Fig. 2 summarizes the number of rock samples in different regions and rock types. The carbonate rock samples included in the dataset are mainly from 5 countries or regions. They are the USA (173), Denmark (69), Middle East (13), France (9) and Indonesia (2). Limestone and dolomite are major types of carbonate rocks. The fractions of limestone and dolomite among effective imbibition tests are 55% and 39%, respectively. Most dolomite samples are provided in the USA. They are obtained from Fuhrman-Masho field in Texas, Cottonwood Creek field in Wyoming, Thornton Quarry field in Illinois, Dagger Draw field in New Mexico, Lustre field in Montana, and Copper Ridge field in Ohio. In contrast, the Stevns Klint near Copenhagen, Denmark provides the largest fraction of limestone samples. Meanwhile, limestone from Texas Cordova cream limestone, Poitou region in France and Wakamuk field in Indonesia are applied to prepare rock samples.

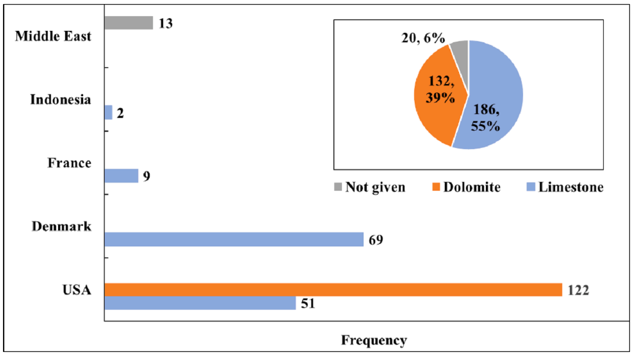

Fig. 2. Distribution of carbonate rock samples based on regions and rock types.

3. Data analysis methods

After dataset construction, descriptive statistical analysis is utilized to implement data analysis. This technique could provide both summary statistics and simple graphs to describe the dataset [19,73]. In general, the detailed methods are summarized as follows: (1) A combination plot consists of stacked histogram and line plot is created to better illustrate information (e.g., Fig. 4). The purpose of stacked histogram is to display distribution patterns and identify suitable ranges of important parameters in limestone and dolomite. Cumulative percentage curve is used to show the percentage of imbibition tests conducted in a certain parameter range. In addition, the gap between cumulative percentage curves of limestone and dolomite could clearly indicate the difference between these two rock types. (2) A boxplot is utilized to detect outliers or special cases for each parameter. The five-number summary includes minimum, first quartile (Q1), median, third quartile (Q3), and maximum values. The lower limit and upper limit are determined by [Q1 − 1.5*(Q3-Q1)] and [Q3 + 1.5*(Q3-Q1)]. All points outside this range are plotted as outliers and regarded as special cases. All special cases are checked carefully and corrected from relevant data sources if needed. Fig. 3 indicates a typical boxplot with each element labelled. (3) Different from histogram, a bar chart is a graphical display of categorical parameters (e.g., Fig. 9). It compares distribution among discrete categories. (4) A scatter plot is applied to display values of two parameters, or three parameters if one parameter is colored or shaped (e.g., Fig. 5). It is preferred to reveal the correlations between parameters.

4. Application guidelines

4.1. Rock properties

Porosity. Wettability alteration induced by surfactants has been implemented effectively in both limestone and dolomite. Yet there are noticeable differences between distributions of porosity between them (see Fig. 4a). The porosity of dolomite is smaller than 40%, where almost all porosity is less than 30% as indicated from cumulative percentage curve. The range from 10 to 20% is the peak range, which accounts for more than 60% of imbibition tests. On the other hand, a more symmetric distribution is observed in limestone. Most of imbibition tests fall into

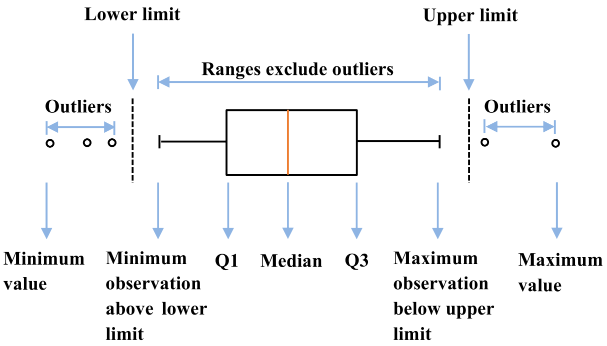

Fig. 3. Schematic of boxplot with outliers.

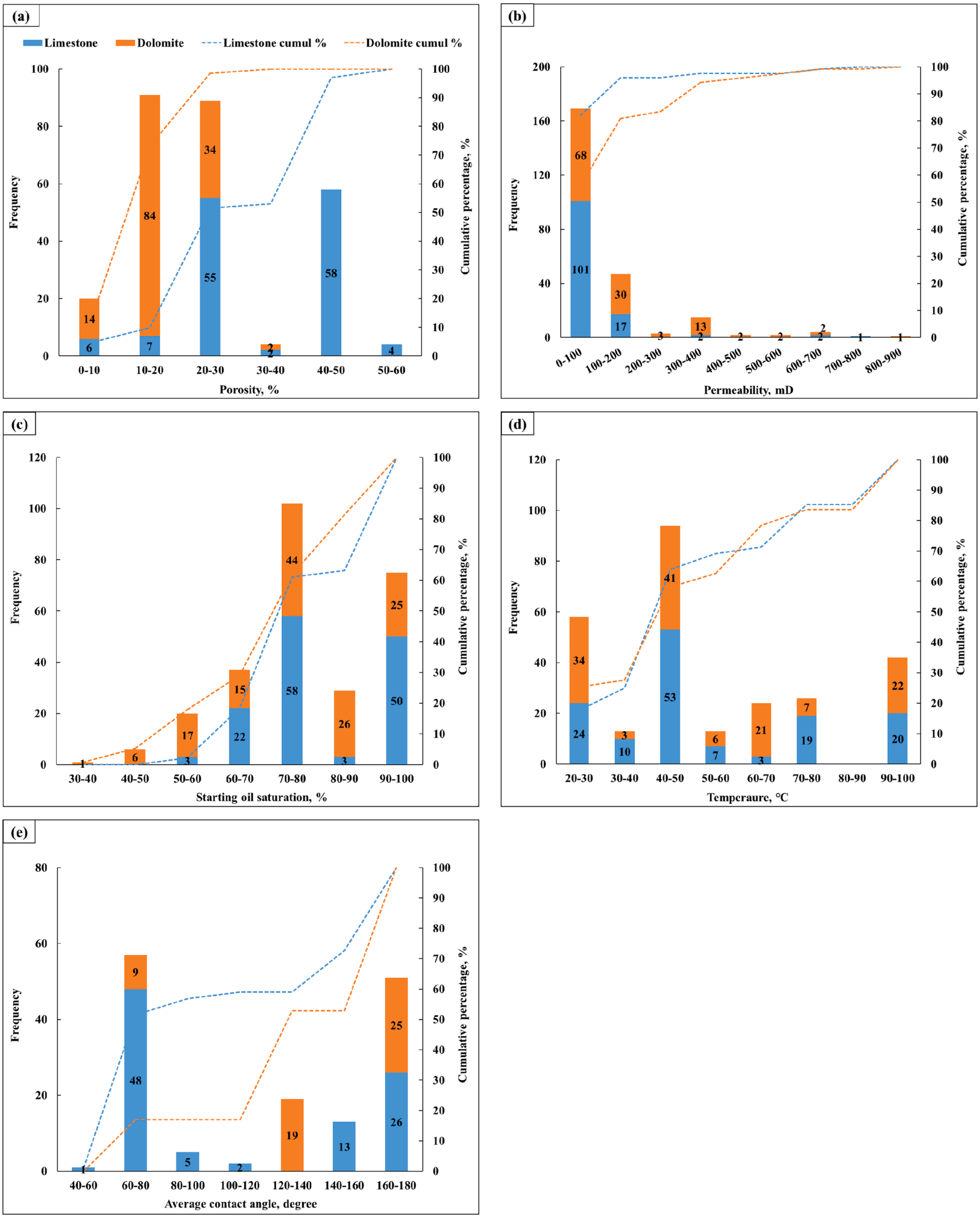

Fig. 4. Distribution of (a) porosity, (b) permeability, (c) starting oil saturation, (d) temperature, and (e) average contact angle based on rock types. The number inside each bar represents the number of samples located in a certain parameter range. Dotted line represents cumulative percentage of samples located in a certain parameter range. Given a parameter range, the difference between numbers inside the bar and the gap between cumulative percentage curves indicate the distribution difference between limestone and dolomite.

ranges from 20 to 30%, and 40 to 50%. Moreover, the number of imbibition tests in these two ranges are very close. It is of interest that limestone with porosity larger than 40% is chalk, which is gathered from the Stevns Klint close by Copenhagen, Denmark [51,62,64,65,67,68].

Permeability. Permeability can be measured through gas or liquid methods. Most permeability values in this dataset are obtained with gas method, hence gas permeability is selected in the next analysis. Weiss and Xie proposed that the permeability should be kept larger than 1 mD to improve oil recovery [24]. While the minimal permeability in the updated dataset is low as 0.04 mD, which is from dolomite in Lustre field, Montana [70]. As indicated in Fig. 4b, the permeability covers a broad range from 0.04 up to as high as 900 mD, and the great variation is

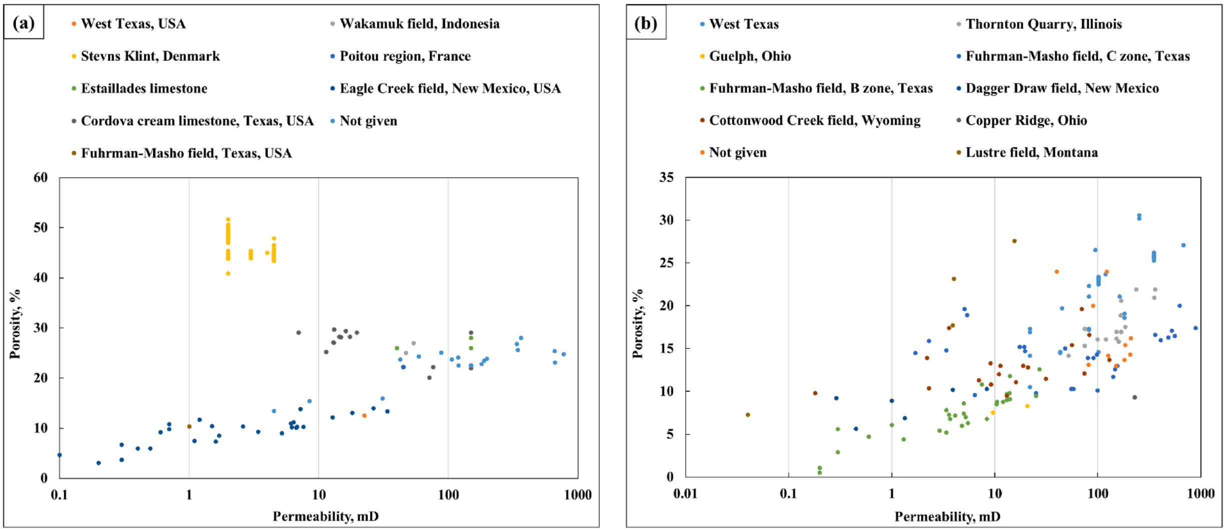

Fig. 5. Relationship between porosity and permeability in (a) limestone, and (b) dolomite.

thought to be mainly attributed to natural fractures in carbonate rocks. The distribution is much similar between limestone and dolomite. Overall, more than 80% of imbibition tests are implemented with permeability smaller than 200 mD. The permeability is relatively high in carbonates from Middle East [54] and Fuhrman-Masho field, Texas, USA [24]. By contrast, the permeability of chalk provided from Denmark is often less than 10 mD [64,65,68].

The correlation between permeability and porosity of carbonate rocks is indicated in Fig. 5, which shows a complex relationship. In general, the permeability is positively correlated with porosity in both limestone and dolomite. Yet there are carbonate rocks which present high porosity but low permeability, or vice versa. For example, the chalk collected from Denmark has porosity in the range 40–55% and permeability in the range 1–10 mD. This material is utilized to represent the Ekofisk formation in the North Sea, which is a typical chalk reservoir with characteristics of oil-wetness, low permeability, and high porosity [51,62]. As stated by Bohnsack et al., the relationship between permeability and porosity showed dependency on stratigraphy, lithology, and facies [74]. The complexity of the relationship has been thought to be caused by sedimentary and diagenetic environment [75–77].

Starting oil saturation. Generally, carbonate rocks could be saturated either with 100% initial oil saturation or with connate water saturation. For each type of saturation status, surfactant imbibition tests are implemented in either secondary phase or tertiary phase. Fig. 4c illustrates the distribution of oil saturation when surfactant imbibition tests are started. The oil saturation covers from 30 to 100%, and the range between 70 and 80% is observed with most frequency. The maximal oil saturation indicates surfactant imbibition tests are conducted with 100% oil-saturated carbonates in secondary phase. In contrast, the minimal oil saturation shows surfactant imbibition tests are conducted with carbonates with initial water saturation in tertiary phase.

Temperature. Many properties of surfactants show considerable relevance with temperature, including critical micelle concentration (CMC) value, surfactant diffusivity, surfactant adsorption on rock surface, and thermal stability. Nonionic surfactants are especially sensitive to temperature, which could start to phase-separate and become cloudy at temperature higher than their cloud points. It is shown that the wettability tends to be more water-wet at increasing temperature. The trend results from mixed mechanisms, which includes the change of IFT, the reduction in oil viscosity, the change of fluid density, as well as thermal gradient [78]. As illustrated in Fig. 4d, surfactants are capable to alter wettability in a wide temperature range from 20 to 100 °C, and 40–50 °C as the peak range. The lowest temperature is close to room temperature, which is set to model a reservoir temperature [40]. On the other hand, the highest temperature is mainly applied to screen promising surfactants at high-temperature carbonate reservoirs. It is challenging to design effective surfactant systems in this type of carbonate reservoirs. Moreover, the criterion of high temperature keeps on increasing. It has increased from 70 to 90 °C [45], higher than 90 °C [5], to 100 °C or above [48]. The target carbonate reservoirs are mainly located in Middle East region [34,79].

Average contact angle. In literature, multiple techniques have been applied to measure or describe the wettability of carbonate rocks. A comprehensive review of these techniques has been included in our recently published review paper [15]. The contact angle is applied to quantify the wettability in this paper because it is the most widely used indicator. The average contact angle covers the range from 55 to 180°. Although the available data is limited, peak distributions are found in the range 60 – 80° and 160 – 180° (see Fig. 4e). The average contact angle in the range 60 – 80° is measured on mineral plate surface, which is mainly aimed to improve wettability alteration efficiency in Ekofisk chalk formation in the North Sea [44,56,65,68]. The average contact angle in the range 160 – 180° is measured on either mineral plate surface or core plug surface, which is to study wettability alteration in Cordova cream limestone (Texas) [43,45–47], Guelph dolomite (Ohio) [5], and Silurian dolomite (Illinois) [5,50,52].

4.2. *Oil properties*

Dead oil, simulated oil and commercial oil have been applied to model crude oil in imbibition tests. Based on constructed dataset, the fractions of these three categories of oil are 62%, 33% and 5%, respectively. Dead oil is defined as oil where gas and volatile hydrocarbons are removed. Simulated oil could be made from dead oil by dilution with light organic components. Heptane and low equivalent alkane carbon number (EACN) hydrocarbon are often served as light components in literature [5,48,65,69]. On the other hand, commercial oil consists of organic compounds, which includes aliphatic hydrocarbons [37,62,64,65,71], carboxylic acids dissolved in heptane [62], and naphthenic acids dissolved in decane [47,72]. Since the composition is different among them, the properties vary as well. First, the oil API gravity increases generally in the order, dead oil < simulated oil < commercial oil (see Fig. 6a). Second, oil viscosity measured at experimental temperature presents an opposite trend to gravity (see Fig. 6b). Third, acid number is a good indicator to quantify fractions of fatty acids and carboxylate anions in oil, and it has been utilized to denote oil-wetness degree [80]. A higher acid number can induce a more oil-wet state [81–83]. As indicated in Fig. 6c, most dead oil and commercial

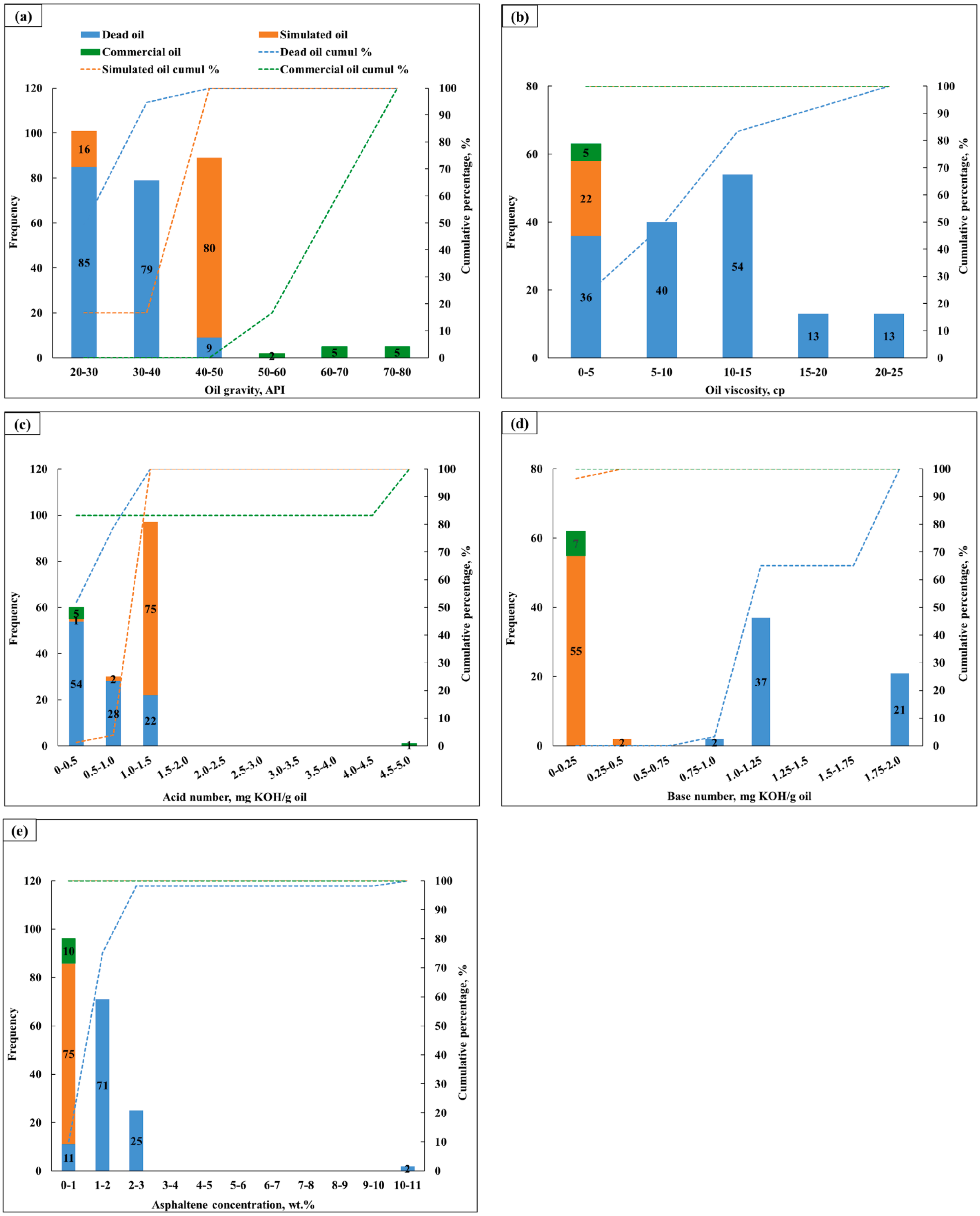

Fig. 6. Distribution of (a) gravity, (b) viscosity, (c) acid number, (d) base number, and (e) asphaltene concentration based on oil types.

oil samples have acid number smaller than 1.0 mg KOH/g oil, while simulated oil samples mainly fall into the range from 1.0 to 1.5 mg KOH/g oil. Fourth, the basic compounds could react with acidic compounds to form acid-base complexes, which has been indicated to prevent acidic compounds adsorbing on carbonate rocks surface. A higher base number could induce a more water-wet state [84]. As shown in Fig. 6d, simulated oil and commercial oil are found with lower base number than dead oil. Fifth, polar components from asphaltenes have been documented to show high surface activity in rendering carbonate rocks surface to oil-wet [85–88]. For some oil samples, asphaltene concentration shows a positive correlation with acid number [64]. Simulated oil and commercial oil are found with less asphaltene than dead oil (see Fig. 6e). As the oil API gravity increases, the oil solvency to asphaltene becomes poorer and the amount of asphaltene in oil decreases. A negative correlation has been revealed between oil API gravity and asphaltene concentration in Fig. 7.

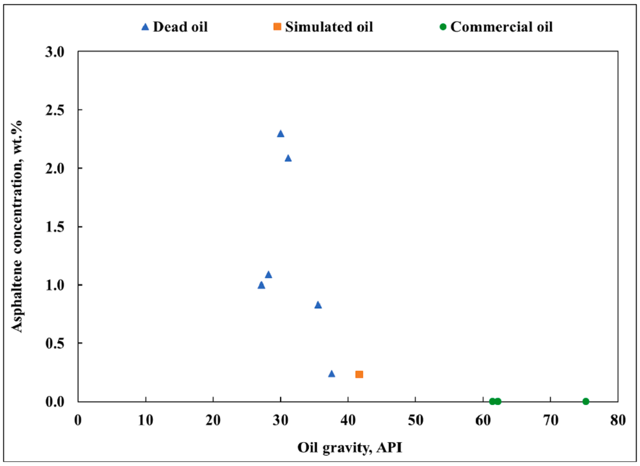

Fig. 7. Relationship between asphaltene concentration and oil gravity for various types of oil.

Fig. 8 indicates both histogram and cumulative percentage curve for key oil properties in regard to rock types. They could assist in revealing distribution of oil properties in limestone and dolomite.

Oil gravity. Based on the classification of oil by Meyer et al., light oil and medium oil are characterized with API gravity larger than 25° and 20 to 25° inclusive [89]. As shown in Fig. 8a, the least oil gravity is larger than 20 °API, imbibition tests are therefore implemented with light to medium oil. In terms of rock types, the distribution in limestone differs greatly from dolomite. The oil gravity in dolomite is distributed in the range from 20 to 50 °API, while the range extends to 20 and 80 °API in limestone. The content of imbibition tests with oil gravity greater than 50 °API is about 10%, where commercial oil is applied.

Oil viscosity. As presented in Fig. 8b, oil viscosity is less than 25 cp. This finding is consistent with criteria proposed by Taber and Martin, where surfactant EOR is suggested to apply with low-to-medium viscous oil [17]. Compared with oil gravity, a more even distribution is observed in oil viscosity.

Acid number. Nearly all imbibition tests are observed to have acid number smaller than 1.5 mg KOH/g oil (see Fig. 8c). Only one imbibition test is implemented in limestone, where the saturated oil has an acid number 4.5 mg KOH/g oil [72]. Moreover, cumulative percentage curves in limestone and dolomite are close, which indicates the distribution in such two types of rocks are comparable. The range from 1.0 to 1.5 mg KOH/g oil has the most frequency in both limestone and dolomite.

Base number. There are large differences between the distributions of base number in limestone and dolomite (see Fig. 8d). The base number in limestone is lower than 1.25 mg KOH/g oil, and the range with the most frequency is lower than 0.25 mg KOH/g oil. On the other hand, the base number in dolomite is mainly in the range from 1.75 to 2.0 mg KOH/g oil.

Asphaltene concentration. In general, the distribution of asphaltene concentration is likewise with acid number. The asphaltene concentration of almost all imbibition tests ranges from 0 to 3 wt%, while two imbibition tests are conducted with oil where the asphaltene concentration is 10.7 wt% [37]. In addition, the range between 0 and 1 wt% is found as the peak range.

4.3. Water properties

In surfactant imbibition tests, there are two categories of water and functions of them are various. Connate water herein is utilized to saturate carbonate rocks to serve the role of formation water. On the other hand, imbibition water is used to prepare surfactant solutions which could be imbibed into porous media to displace oil. Fig. 9 compares water types distributed in connate water and imbibition water. Synthetic water, formation water and deionized water have been applied as connate water. On the other hand, imbibition water is composed of five categories of water, namely deionized water, formation water, produced water, seawater, and synthetic water. Synthetic water is the peak water type which occupies about 94% of imbibition water samples. This trend is observed in connate water as well. Produced water and seawater have been applied as imbibition water while not as connate water [53]. The synthetic water consists of synthetic formation water, synthetic produced water, synthetic seawater, and electrolytes solution. Among them, synthetic formation water is appealing substitute for formation water, and it has the most frequency in both imbibition water and connate water to simulate reservoir conditions. In general, imbibition water can be either remained same or different from connate water. In view of established dataset, imbibition water is kept same with connate water in 60% of imbibition tests, while differs from connate water in 40% of imbibition tests.

Salinity. It has been proved that the CMC value, surfactant adsorption, aqueous stability of surfactants, phase behavior of surfactants, contact angle, and oil/water IFT are considerably dependent on salinity. Thus, salinity is a crucial water parameter for surfactant huff-puff treatments. Fig. 10 shows the distribution of salinity in connate water and imbibition water. The salinity of connate water covers a wide range between 0 and 225 g/l, where more than 90% of connate water samples fall into the range less than 125 g/l. This indicates imbibition tests are implemented effectively in both low salinity and high salinity carbonate rocks. The lowest salinity of connate water is 0 g/l, which is from deionized water [31,67,72]. The highest salinity of connate water is approximate 214 g/l, which is from either formation water or synthetic formation water. These investigations are conducted to improve wettability alteration efficiency at high salinity carbonate reservoirs. However, in these investigations, the imbibition water is prepared by seawater, produced water, and synthetic water, where the salinity is in the range from 57 to 68 g/l [49,53,54]. Compared with connate water, the salinity range narrows to 0 and 125 g/l in imbibition water, and more than 80% of imbibition water samples fall into the range less than 50 g/l.

Divalent cations concentration. Divalent cations often refer to calcium (Ca^{2+}) and magnesium (Mg^{2+}) ions. The content of divalent cations determines the hardness of water. Water becomes harder with increase of divalent cations concentration. The water hardness is of particular importance to select suitable types of surfactants. Anionic surfactant molecules are reported to react with divalent cations, as a result, the amount of active surfactant molecules in wettability alteration is decreased [5,50]. A similar distribution is found in divalent cations concentration with salinity. As indicated in Fig. 11a, the divalent cations concentration in connate water covers from 0 to 22.5 g/l, and the range less than 5 g/l accounts for more than 90% of connate water samples. The minimal divalent cations concentration in connate water is from deionized water [31,67,72] and electrolytes solution including NaCl (aq), KCl(aq), Na_2CO_3(aq), NaCl & Na_2CO_3(aq) [33,36,37]. The maximal divalent cations concentration in connate water is close to 22 g/l, which is from synthetic formation water with high hardness. However, the corresponding divalent cations concentration in imbibition water is close to 3 g/l [49,53,54]. In general, divalent cations concentration in imbibition water is in the range between 0 and 5 g/l.

It is worthy to mention that a synthetic formation water with salinity 263.7 g/l and divalent cations concentration 24.6 g/l has been used as connate water [34]. This research is to screen effective surfactants at high temperature, high salinity (HTHS) carbonate reservoirs located in Middle East. Yet the detailed carbonate rock type is not given in literature.

A summary of application guidelines for wettability alteration with surfactants constructed on statistical analysis is given in Table 2. Rock types, important rock, oil, and water properties are contained in these guidelines. For each parameter, summary statistics information includes

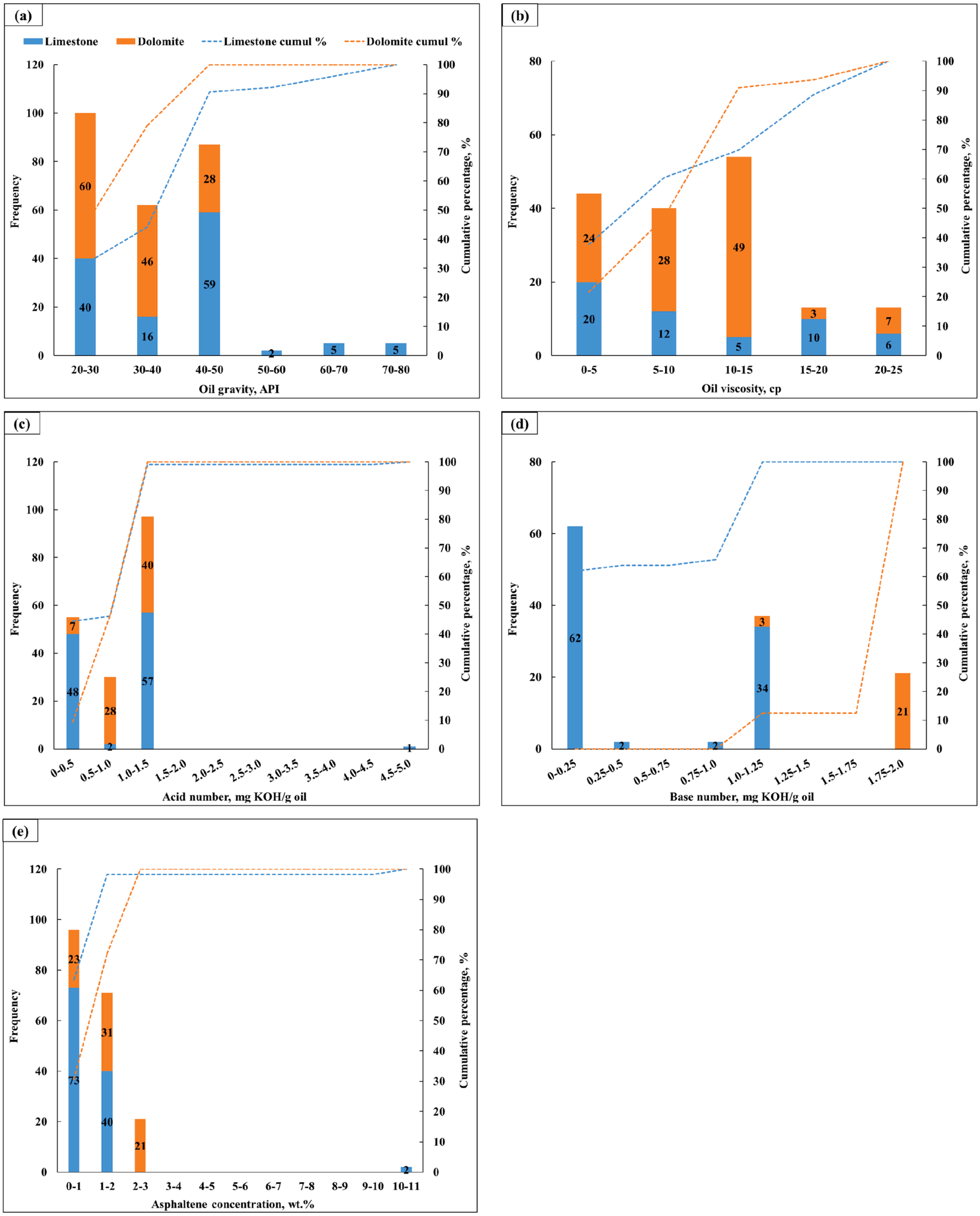

Fig. 8. Distribution of (a) gravity, (b) viscosity, (c) acid number, (d) base number, and (e) asphaltene concentration based on rock types.

mean, minimum, median, and maximum are listed. Apart from that, an applied range developed from boxplots is provided to detect outliers or special cases. It is worth paying attention to a new datum if it is beyond this range. The new datum can be either special rock/fluid case or a newly applicable condition for surfactant huff-puff treatments. The analysis results are the first application guidelines for wettability alteration with surfactants in literature.

5. Design considerations for surfactant huff-puff treatments

5.1. Surfactant systems

It has been documented that anionic, cationic, nonionic, zwitterionic, and gemini surfactants have been utilized to alter the wetting state of carbonate rocks. Either single surfactant or mixture of several surfactants could be applied. Fig. 12 summarizes the distribution of various surfactant systems based on rock types. In terms of single surfactant,

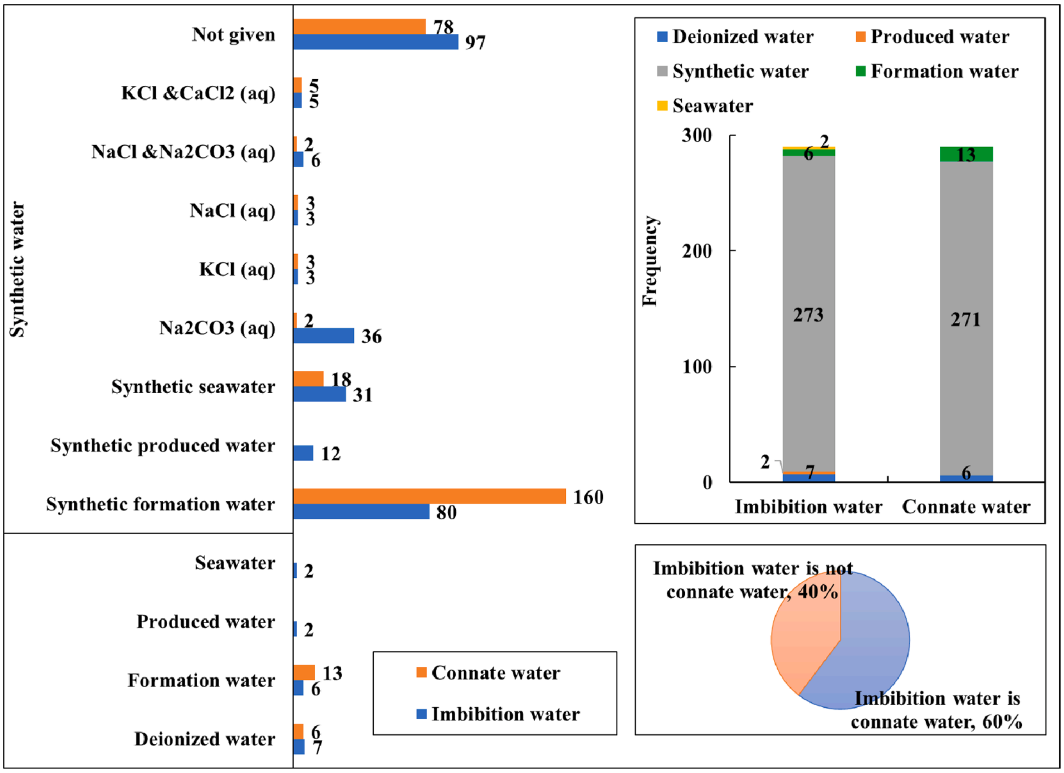

Fig. 9. Distribution of water types in connate water and imbibition water.

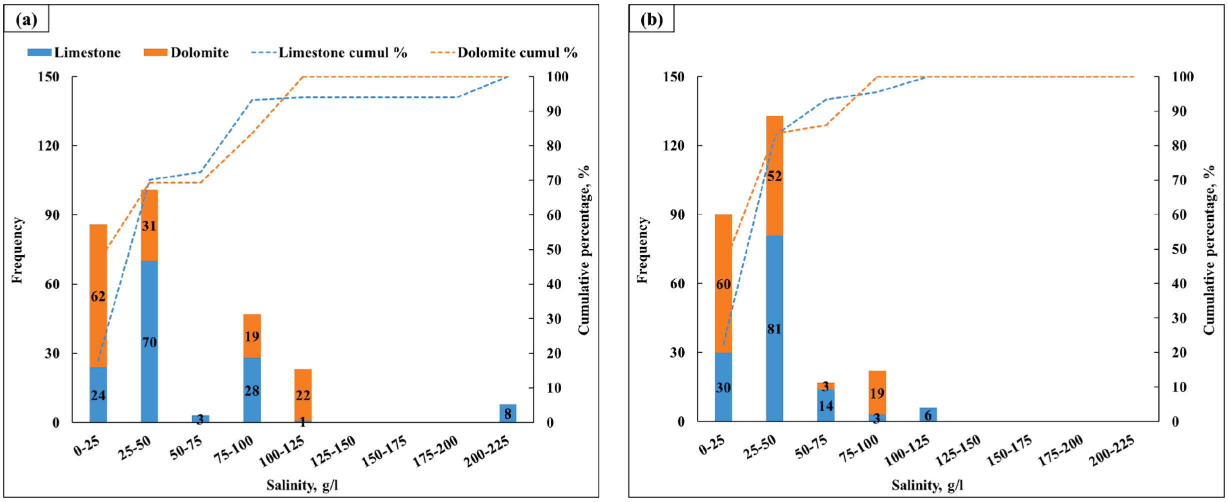

Fig. 10. Distribution of salinity in (a) connate water and (b) imbibition water based on rock types.

anionic, cationic and nonionic surfactants have the most frequency, which accounts for 83% of imbibition tests. Anionic surfactants often contain sulfates or sulfonates as hydrophilic groups. The commonly used cationic surfactants include quaternary ammonium salts, phosphonium salts, and alkyl amines. Yet the frequently applied nonionic surfactants are polyoxyethylene alcohol, ethoxylated alcohol, and nonylphenoxypoly (ethyleneoxy) ethanol. Cationic surfactants are favoured by many researchers, and they have been applied as wettability alteration agents in 36% of imbibition tests. In addition, cationic surfactants are mostly used in both limestone and dolomite. The appealing features of cationic surfactants include strong and irreversible wettability alteration effect, high thermal and aqueous stability, excellent tolerance to hard brines, and low adsorption [5,43,52,65,90]. On the contrary, 4% of imbibition tests have been implemented with zwitterionic surfactants. This can be ascribed to the high cost of zwitterionic surfactants which limits their wide applications [91]. Gemini surfactants are relatively new and show desirable prospects in wettability alteration applications. Gemini surfactants present advantages over conventional surfactants in several ways, including lower CMC value and adsorption on rock surface [92,93], high performance in obtaining ultralow IFT [94], together with better wetting, solubilizing and rheological properties [95]. Yet only few applications with gemini surfactants are available in literature, and the fraction is about 1%.

For imbibition tests with blends of surfactants, the fraction is about 12%. The blends consist of several surfactants which are from either same type or different types. The blends are capable to improve wettability alteration performance and extend applicable conditions of individual type of surfactants. First, blends composed of several anionic

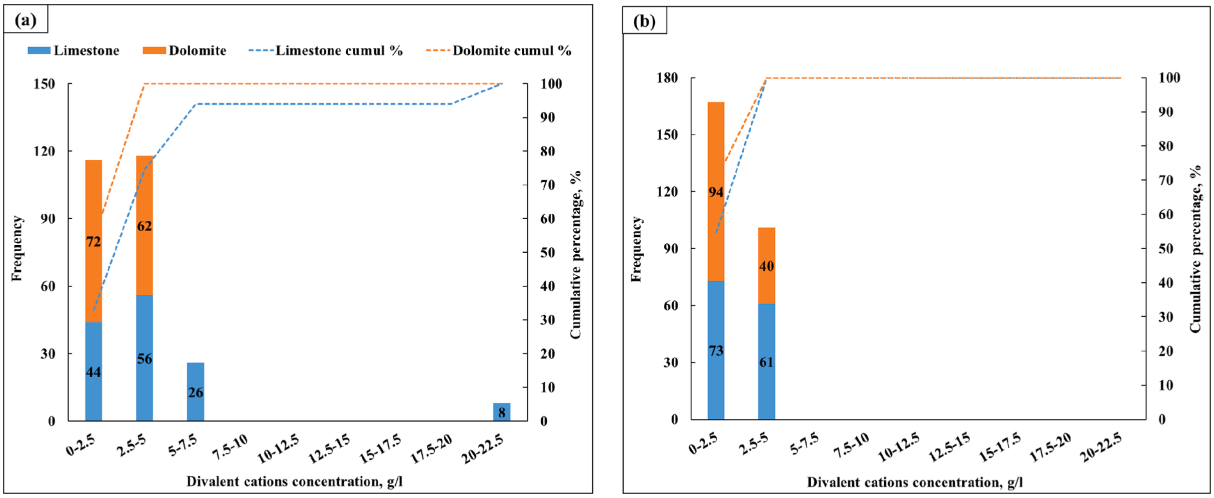

Fig. 11. Distribution of divalent cations concentration in (a) connate water and (b) imbibition water based on rock types.

Table 2
Guidelines for wettability alteration with surfactants in carbonate rocks.

Parameters	Rock types	Ranges exclude special cases	Mean	Minimum	Median	Maximum
Porosity, %	Dolomite	5.6–30.6	16.7	5.6	16.1	30.6
	Limestone	3.1–51.7	33.8	3.1	29.5	51.7
	Overall	3.1–50.0	25.1	3.1	22.9	51.7
Permeability, mD	Dolomite	0.04–360.0	132.3	0.04	86.5	887.0
	Limestone	0.2–106.0	53.2	0.20	4.5	775.0
	Overall	0.04–364.0	120.4	0.04	31.2	1458.0
Starting oil saturation, %	Dolomite	40.9–99.2	75.2	37.7	74.9	99.2
	Limestone	55.0–100.0	81.5	55.0	74.9	100.0
	Overall	37.7–100.0	77.3	37.7	74.4	100.0
Temperature, °C	Dolomite	20.0–100.0	50.5	20.0	40.0	100.0
	Limestone	22.0–92.0	49.0	22.0	40.0	92.0
	Overall	20.0–100.0	52.4	20.0	40.0	100.0
Average contact angle, °	Dolomite	132.6–180.0	138.2	68.0	133.0	180.0
	Limestone	55.0–173.0	112.9	55.0	78.0	173.0
	Overall	55.0–180.0	120.8	55.0	133.0	180.0
Oil gravity, °API	Dolomite	27.1–30.4	31.6	22.0	30.0	44.8
	Limestone	27.1–61.4	39.2	27.1	41.7	75.2
	Overall	22.0–61.4	35.0	22.0	30.4	75.2
Oil viscosity, cp	Dolomite	9.9–12.4	10.3	1.4	10.0	22.5
	Limestone	0.3–23.0	10.7	0.3	9.9	23.0
	Overall	0.3–23.0	9.6	0.3	9.9	23.0
Acid number, mg KOH/g oil	Dolomite	0.20–1.04	0.79	0.20	1.00	1.04
	Limestone	0.00–1.04	0.67	0.00	1.04	4.50
	Overall	0.00–1.04	0.71	0.00	1.00	4.50
Base number, mg KOH/g oil	Dolomite	1.83–1.83	1.75	1.17	1.83	1.83
	Limestone	0.00–1.17	0.42	0.00	0.01	1.17
	Overall	0.00–1.83	0.68	0.00	0.13	1.83
Asphaltene concentration, wt.%	Dolomite	0.23–2.3	1.13	0.23	1.00	2.3
	Limestone	0.00–1.09	0.72	0.00	0.23	10.7
	Overall	0.0–2.3	0.91	0.00	1.00	10.7
Salinity of connate water, g/l	Dolomite	0.0–118.1	41.9	0.0	30.8	118.1
	Limestone	0.0–100.0	55.4	0.0	44.9	213.6
	Overall	0.0–118.1	58.8	0.0	44.9	263.7
Divalent cations concentration of connate water, g/l	Dolomite	0.0–4.0	2.1	0.0	1.8	4.0
	Limestone	0.0–6.2	4.6	0.0	4.4	21.5
	Overall	0.0–6.2	4.4	0.0	3.4	24.6
Salinity of imbibition water, g/l	Dolomite	0.0–77.9	29.7	0.0	30.8	77.9
	Limestone	8.0–66.9	38.5	0.0	35.5	106.0
	Overall	0.0–90.0	36.8	0.0	32.3	263.7
Divalent cations concentration of imbibition water, g/l	Dolomite	0.0–3.4	1.7	0.0	1.0	3.4
	Limestone	0.0–4.4	2.1	0.0	1.8	4.4
	Overall	0.0–5.3	2.1	0.0	1.8	24.6

surfactants have been observed to show advantages in multiple aspects: enhance aqueous stability in hard brines [46]; tune optimal salinity to achieve lowest IFT at target conditions [96]; as well as make up the quality variety arises in production process [97]. Second, cationic surfactants are appealing agents to alter wettability while anionic surfactants are appealing agents to lower IFT. Cationic-anionic surfactant system is designed to acquire a synergy between wettability alteration and IFT reduction. It has been shown that the oil recovery from this mixture is higher than those from cationic or anionic surfactants alone [52]. Third, the CMC value and IFT from blends of different cationic

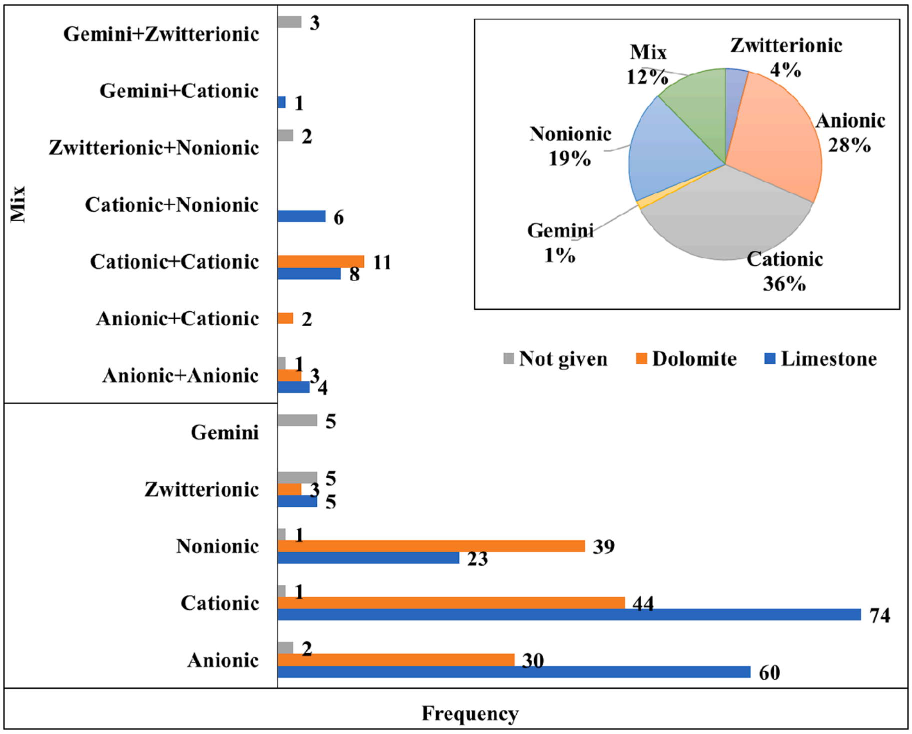

Fig. 12. Distribution of surfactant systems.

surfactants are lower than those from individual surfactant alone [51]. Hence, the wettability of carbonate rocks can be altered to more water-wet and higher oil recovery can be achieved. Fourth, the application of nonionic surfactants in high temperature conditions is mainly limited by their cloud points. It has been documented that addition of cationic surfactants to nonionic surfactants solution can enhance thermal tolerance [49]. In combination with good performance of nonionic surfactants in high salinity conditions, this nonionic-cationic system has been regarded as good candidate for HTHS carbonate reservoirs. Fifth, in practical applications, co-surfactants could be necessary to improve properties and effectiveness of main surfactant solutions. The roles of co-surfactants include reducing IFT, adjusting hydrophilic-lipophilic balance (HLB) and assisting in forming microemulsion [98]. For example, nonionic surfactants have been served as co-surfactants in zwitterionic surfactants solution as indicated by Han et al [53]. Lastly, conventional surfactants could be applied together with gemini surfactants to gain synergistic effects. Cationic-gemini surfactant system has been documented by Qi et al [54], and zwitterionic-gemini surfactant system has been investigated by Ghosh and Mohanty [99].

Table 3 summarizes the application guidelines for anionic, cationic, and nonionic surfactants. This table reveals several important findings for screening a feasible surfactant type for a given candidate reservoir. First, the average temperature where nonionic surfactants are applied is lower than anionic and cationic surfactants. Furthermore, a temperature higher than 60 °C is detected as a special case for nonionic surfactants, while the limit is increased to 75 and 100 °C for cationic and anionic surfactants, respectively. The cloud point is a key factor which limits the thermal stability of nonionic surfactants in high temperature conditions. Second, the imbibition water salinity for nonionic surfactants is generally higher than anionic and cationic surfactants, which is reflected in the mean, median, maximum, and upper limit to detect special cases. The aqueous stability of ionic surfactants needs to be evaluated in high salinity conditions. Third, anionic surfactants should be applied with caution in high divalent cations concentration conditions. It is shown that the average divalent cations concentration where anionic surfactants are used is 0.7 g/l, whereas the value is increased to>2.0 g/l for cationic and nonionic surfactants. Besides that, the upper limit to detect special divalent cations concentration for anionic surfactants is 2.2 g/l, while the limit is increased to 3.4 and 4.4 for nonionic and cationic surfactants, respectively.

5.2. *Surfactant concentration*

Surfactant concentration is of great interest to the design of surfactant systems. Extent of wettability alteration, imbibition rate and improved oil recovery show correlations with surfactant concentration. A critical surfactant concentration is expected to exist where the best performance is observed. Below this critical concentration, more water-wet state, higher imbibition rate and improved oil recovery are observed with increase of concentration. The effect of concentration becomes weak when the critical concentration is exceeded. The critical concentration has been reported to be higher than CMC, hence concentration above CMC is favorable in practical applications. This setting is rewarding in multiple ways: maximal content of surfactant monomers, lowest IFT, and compensation for surfactant loss caused by adsorption. Fig. 13 gives a clear distribution of surfactant concentration with respect to limestone and dolomite. A wide range is observed, which covers from near 0 up to 5.0 wt%. Nearly all imbibition tests fall into the range<2.0 wt%, and the peak range is<1.0 wt%. The lowest concentration is 0.01 wt%, where a cationic surfactant with a low CMC is utilized as wettability alteration agent [70]. On the other hand, concentration>2.0 wt% is mainly from surfactants with comparatively high CMC [31,32,36,65]. It is worthy to mention that the highest concentration is far higher than CMC, and it is set to study the influence of concentration on oil recovery [65]. The imbibition rate is faster at 5.0 wt% than 1.0 wt%, whereas the ultimate oil recovery is much similar in both cases.

5.3. *Additive information*

In practical applications, additives can be applied to improve the efficiency of surfactants. Table 4 provides an overview of reported additives in literature. Based on mechanisms of additives, additives can be categorized into chelating agents, pH control agents, and co-solvents. First, chelating agents are commonly applied in anionic surfactant

Table 3
Guidelines for wettability alteration in carbonate reservoirs based on surfactant types.

Parameters	Surfactant types	Ranges exclude special cases	Mean	Minimum	Median	Maximum
Porosity, %	Anionic	3.1–29.7	21.7	3.1	22.2	44.9
	Cationic	5.6–51.7	32.1	5.6	42.3	51.7
	Nonionic	3.7–31.3	17.7	3.7	16.3	31.3
Permeability, mD	Anionic	0.2–236.0	86.1	0.2	74.6	236.0
	Cationic	0.2–74.2	63.6	0.2	4.5	1320.0
	Nonionic	0.3–181.0	102.3	0.3	18.4	887.0
Starting oil saturation, %	Anionic	61.6–87.4	77.3	55.0	73.0	100.0
	Cationic	40.9–100.0	82.7	40.9	82.0	100.0
	Nonionic	40.9–100.0	83.9	37.7	82.4	100.0
Temperature, °C	Anionic	20.0–100.0	57.4	20.0	40.0	100.0
	Cationic	20.0–75.0	46.8	20.0	40.0	100.0
	Nonionic	20.0–60.0	42.4	20.0	40.0	100.0
Average contact angle, °	Anionic	132.6–180.0	155.6	55.0	165.0	180.0
	Cationic	68.0–78.0	86.9	55.0	75.0	165.0
	Nonionic	133.0–173.0	131.3	55.0	133.0	173.0
Oil gravity, °API	Anionic	22.0–45.2	32.8	22.0	28.2	62.1
	Cationic	22.0–47.6	39.8	22.0	41.7	75.2
	Nonionic	27.1–30.4	29.6	27.1	27.7	44.8
Oil viscosity, cp	Anionic	2.9–23.0	11.9	2.9	10.0	23.0
	Cationic	0.3–12.4	8.5	0.3	12.3	12.4
	Nonionic	9.7–12.4	9.7	1.4	9.9	23.0
Acid number, mg KOH/g oil	Anionic	0.08–1.04	0.5	0.08	0.2	4.5
	Cationic	0.0–1.04	1.1	0.0	1.0	4.5
	Nonionic	0.2–1.0	1.4	0.2	1.0	4.5
Base number, mg KOH/g oil	Anionic	1.2–1.2	0.9	0.0	1.2	1.2
	Cationic	0.0–1.8	0.8	0.0	0.01	1.8
	Nonionic	1.2–1.8	1.4	1.2	1.2	1.8
Asphaltene concentration, wt.%	Anionic	1.1–1.1	1.5	0.0	1.1	10.7
	Cationic	0.23–0.23	0.7	0.0	0.23	2.3
	Nonionic	1.0–1.09	1.2	1.0	1.0	2.3
Salinity of connate water, g/l	Anionic	0.0–118.1	59.4	0.0	79.4	118.1
	Cationic	0.0–62.8	37.4	0.0	44.9	213.7
	Nonionic	0.0–118.1	55.4	0.0	77.9	263.7
Divalent cations concentration of connate water, g/l	Anionic	0.0–6.2	3.0	0.0	4.0	6.2
	Cationic	0.0–4.4	3.2	0.0	3.7	21.5
	Nonionic	0.0–6.2	3.2	0.0	2.6	24.6
Salinity of imbibition water, g/l	Anionic	0.0–66.9	35.8	0.0	31.8	106.0
	Cationic	0.0–58.0	31.1	0.0	30.8	100.0
	Nonionic	0.0–77.9	42.7	0.0	35.5	263.7
Divalent cations concentration of imbibition water, g/l	Anionic	0.0–2.2	0.7	0.0	0.0	4.4
	Cationic	0.0–4.4	2.7	0.0	3.4	4.4
	Nonionic	0.0–3.4	2.1	0.0	1.8	24.6

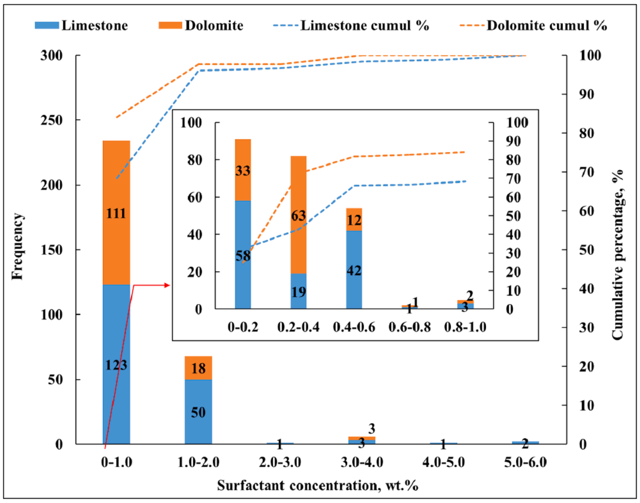

Fig. 13. Distribution of surfactant concentrations.

solutions to avoid divalent cations binding with surfactants. EDTA (ethylene diamine tetraacetic acid) and NaPA (sodium polyacylate) have been reported as chelating agents [5,50,52]. With appropriate usage of them, wettability alteration efficiency and improved oil recovery could be greatly enhanced. Second, the amount of surfactant loss resulted from adsorption on rock surface remains challenging [100]. It is a critical factor in regard to determination of surfactant concentration and economic evaluation of surfactant projects. Among all types of surfactants is anionic surfactants which have a relatively high tendency to adsorb on rock surface. This tendency is mainly caused by the electrostatic attraction force between positively charged rock surface and negatively charged surfactant groups. The pH control agents provide an efficient way to mitigate adsorption problem. On the basis of constructed dataset, Na_2CO_3 and $NaBO_2$ are mainly served as pH control agents. With addition of alkali into surfactant solutions, brine pH can be increased across ZPC of carbonate rocks. Consequently, rock surface becomes more negatively charged and the amount of surfactant molecules adsorbed on rock surface is reduced. Na_2CO_3 is suitable for soft brines with low concentration of Ca^{2+} and Mg^{2+} [40]. In contrast, $NaBO_2$ is efficient in hard brines where $CaCO_3$ and $MgCO_3$ cannot be precipitated [45]. Third, pH control agents and chelating agents have been applied jointly in anionic surfactant solutions as indicated by Kathel and Mohanty [16]. Lastly, because certain surfactants are hardly soluble in aqueous phase, co-solvents are required to improve solubility. EGBE, ethanol and isopropanol are documented as effective co-solvents [31,35,51,68].

5.4. *Water information to prepare surfactant solutions*

As aforementioned in Fig. 9, surfactant solutions can be prepared from deionized water, formation water, produced water, seawater, and

Table 4
Information of additives in surfactant solutions.

Additive types	Surfactant systems	Rock types	Count	References
Chelating agents				
EDTA	Anionic	Dolomite	5	Chen and Mohanty. [5] Chen and Mohanty. [52]
NaPA	Anionic	Dolomite	4	Chen and Mohanty. [5] Chen and Mohanty. [50]
pH control agents				
Na_2CO_3 (In soft brines)	Anionic	Dolomite Limestone	3 41	Tabary et al. [37] Hirasaki and Zhang. [40] Seethepalli et al. [41] Adibhatla and Mohanty. [42] Gupta et al. [43] Gupta et al. [45] Gupta and Mohanty. [46] Gupta and Mohanty. [47] Chen and Mohanty. [5] Chen and Mohanty. [52]
Na_2CO_3 (In soft brines)	Anionic + Anionic	Dolomite Limestone	2 4	Hirasaki and Zhang. [40] Gupta et al. [45] Gupta and Mohanty. [46]
$NaBO_2$ (In hard brines)	Anionic	Limestone	2	Gupta et al. [45]
Chelating agents and pH control agents				
EDTA + Na_2CO_3	Anionic	Limestone	6	Kathel and Mohanty. [16]
Co-solvents				
EGBE	Anionic	Dolomite	2	Sagi et al. [35]
Ethanol	Cationic, Anionic, Anionic + Cationic	Dolomite	3	Valluri et al. [31]
Isopropanol	Cationic + Cationic	Dolomite Limestone	8 4	Strand et al. [68] Standnes and Austad. [51]

synthetic water. Among them is synthetic water that has the most frequency. It is also noticed that Na_2CO_3 (aq) and synthetic seawater have relatively high frequency in imbibition water. Na_2CO_3 (aq) is frequently used as pH control agents in anionic surfactant solutions to decrease surfactant adsorption. Furthermore, the presence of alkali could improve the performance of surfactants. Alkali could release OH^- which reacts with acid components present in crude oil to produce in-situ surfactants to assist in lowering IFT [101]. Also, alkali is capable to ionize organic acids in crude oil, which increases their hydrophilicity and partitioning in water phase [102]. Synthetic seawater contains SO_4^{2-}, Mg^{2+}, and Ca^{2+}, and the ratio of their concentrations is favorable to wettability alteration. Much attention has been paid to individual component and symbiotic interactions among aforementioned ions regarding their wettability alteration effects [80,103–108]. Based on this, several researchers studied the influence of SO_4^{2-}, Mg^{2+}, and Ca^{2+} on the efficiency of surfactants [5,68,106]. Also, the combined wettability alteration effect between surfactants and synthetic seawater has been reported [38,71,109].

As surfactant solutions are imbibed into porous matrix, a new issue needs to be noticed. The surfactant solutions are expected to be diluted by connate water, which can reduce the concentration of surfactants and additives. Apart from dilution, changes could be arisen in salinity, divalent cations content, pH, etc. given that imbibition water properties are not remained consistent with connate water properties. Hence surfactant systems should be carefully designed such that mixed systems are remained active in wettability alteration and IFT reduction especially in the front of imbibition profile. A full assessment of changes in aforementioned parameters is demanded [40]. As proposed by Chen and Mohanty, the ratio of surfactant solutions volume to connate water volume is a good indicator to fulfill above demand. If the volume ratio is kept high in imbibition tests, changes to designed surfactant systems is not obvious [50].

6. Performance evaluation

Wettability alteration and IFT reduction often occur simultaneously in surfactant imbibition tests. Their effects on oil recovery can be influenced by each other. Oil recovery is affected by the coupled effect between wettability alteration and IFT reduction, and it is hard to quantify their contributions to oil recovery [110]. Wettability alteration reverses the direction of capillary force and thus initiates imbibition process. Besides, higher extent of wettability alteration can increase capillary force and enhance the imbibition process [45,52]. On the basis of wettability alteration, the effect of IFT reduction on oil recovery becomes complicated. Lower IFT could weaken the imbibition process since capillary force is decreased. Given that IFT is significantly reduced, the importance of wettability alteration can be limited, and gravitational force becomes more important in driving water phase into rock matrix [38]. The imbibition process controlled by gravitational force is observed to be slower than that controlled by capillary force [45,66]. Yet lower IFT can weaken capillary entrapment, which is beneficial in mobilizing residual oil [66,111]. The coupled effect between wettability alteration and IFT reduction on oil recovery has not been clearly reported in literature. In this paper, we comprehensively evaluate the performance of currently effective surfactant imbibition tests, including wettability alteration, IFT reduction, and oil recovery. We are also studying the coupled effect between wettability alteration and IFT reduction on oil recovery using data analysis methods, and the results will be illustrated in the next paper.

6.1. Wettability alteration and IFT reduction

The extent of wettability alteration can be estimated with comparing the contact angle before and after surfactant addition. It is important to note that contact angle has a relevance on multiple factors not limited to surfactants. In this section, only contact angle measured in the condition where other factors are remained same is used to analyze the effectiveness of surfactants. The reason for this principle is to eliminate the influence of other factors, and to ensure the change of contact angle is caused by surfactants. This principle is applied to IFT data as well. Based on this principle, the amount of data for comparison of contact angle and IFT is markedly decreased.

Fig. 14a illustrates the distribution of contact angle before and after surfactant addition. All data points are located below the diagonal line, which shows the contact angle is decreased and thus the wettability is altered to more water-wet. Because target carbonate reservoirs are different, the initial contact angle varies as well, which is reflected in disperse data points in the horizontal direction. Given the same initial contact angle, several data points fall into a vertical line. This trend indicates that the wettability alteration degree is not kept constant among different tests. This variation is caused by the changes of surfactant properties, which is mainly determined by the research purposes of different reports. These purposes include comparing the wettability alteration efficiency of different surfactant systems, screening surfactants from identical surfactant system, studying the effect of surfactant concentration on wettability alteration, improving the performance of surfactants with additives. The influence of surfactant properties on

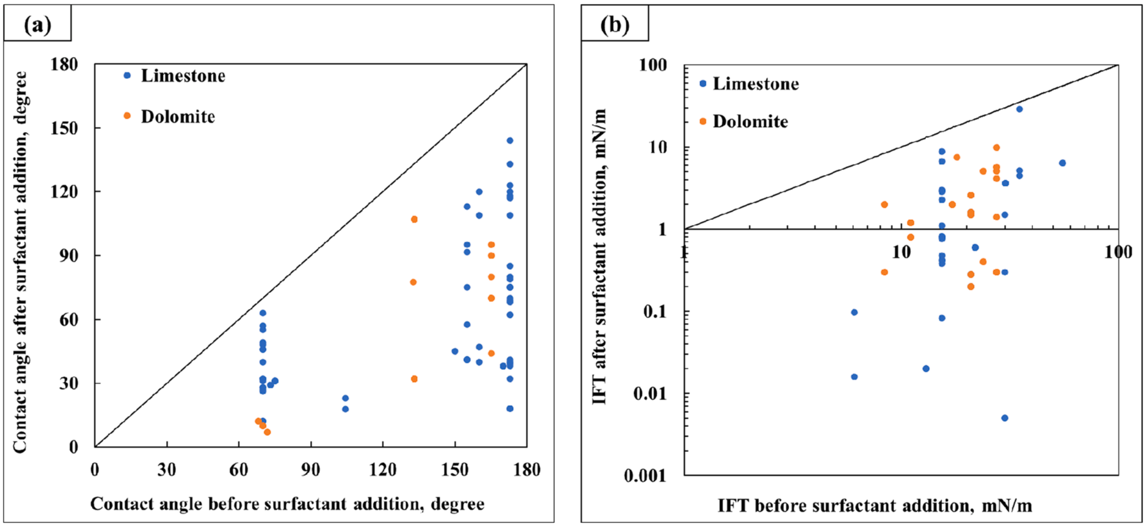

Fig. 14. Change of (a) contact angle and (b) IFT caused by surfactants.

wettability alteration for various surfactant systems has been discussed in detail in our recently published review paper [15]. In general, the contact angle after surfactant addition is in the range from 7° to 144°. The small contact angle is mainly obtained via cationic surfactants, which presents strong and irreversible wettability alteration effect [65].

The comparison of IFT is indicated in Fig. 14b, which shows that IFT is reduced with the usage of surfactants. The initial IFT is mainly related with oil properties, water properties, and temperature. The changes of these factors could result in variations on the initial IFT. The initial IFT covers a range between 6.0 mN/m and 55.4 mN/m. Likewise with contact angle, the degree of IFT reduction varies among tests. This variation can be caused by the changes of surfactant systems, surfactant structures, surfactant concentrations, and additives. The additives herein are alkali, which could react with acid components present in oil to produce in-situ surfactants to aid in reducing IFT [101]. The IFT after surfactant addition covers a wide range from the ultralow IFT ($\sim 10^{-3}$ mN/m) to 29 mN/m. The ultralow IFT is beneficial in reducing capillary entrapment and thus improving oil recovery. In literature, the ultralow IFT is often achieved from middle phase microemulsion, which is formed by optimizing water salinity [33,37,40,41,48,52]. Anionic surfactants are appealing agents to achieve ultralow IFT because of their strong potential in reducing IFT [52]. On the other hand, due to the relatively weak function to reduce IFT, cationic and nonionic surfactants are often applied to obtain high IFT [32]. The highest IFT with 29 mN/m is from a study, which is aimed at investigating the influence of IFT on oil recovery. Both high and low IFT are set in this study [71].

6.2. *Oil recovery*

Surfactant imbibition tests can be conducted either in secondary phase or tertiary phase. In secondary phase, most imbibition tests are conducted directly with surfactants, while fewer water imbibition tests are separately established as baseline cases. The number of surfactant imbibition tests and water imbibition tests are 201 and 28, respectively. In tertiary phase, surfactant imbibition is conducted after water imbibition is ceased. In this way, the number of water imbibition tests equals to the number of surfactant imbibition tests. The number is 115. In this part, the distribution of oil recovery from two phases is discussed.

Secondary phase. Fig. 15a and b show the distribution of oil recovery from water imbibition and surfactant imbibition in regard to limestone and dolomite. Several important conclusions can be revealed in these figures. First, it is interesting to note that the majority of water imbibition and surfactant imbibition tests are implemented with limestone. In water imbibition, only one imbibition test is documented with dolomite. In surfactant imbibition, the number of imbibition tests in limestone and dolomite are 161 and 40, respectively. Second, the oil

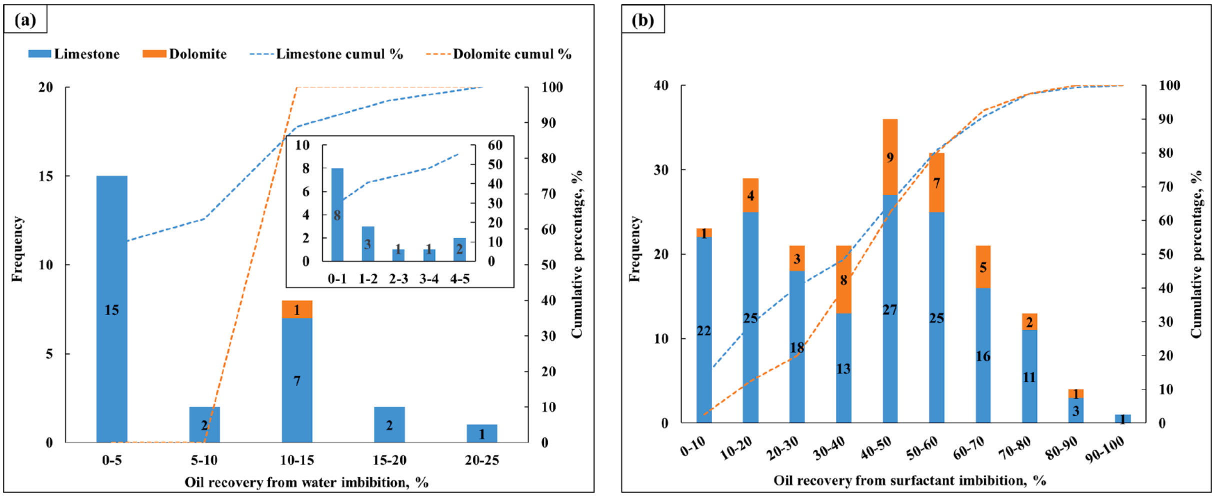

Fig. 15. Distribution of oil recovery from (a) water imbibition and (b) surfactant imbibition.

recovery from water imbibition is<25%, with an average of 7.1%. On the other hand, oil recovery from surfactant imbibition is located in a wide range from nearly 1% to over 90%, with an average of 39.1%. On average, the oil recovery from surfactant imbibition is remarkably higher than that from water imbibition. Also, the wide range of oil recovery implies that the performance of surfactant imbibition varies greatly. The variation is not only caused by surfactants but also relies on properties of rock, oil, water, as well as experimental conditions. The changes of one or more of them can contribute to the alteration of final performance. At last, the peak range of oil recovery from water imbibition is between 0 and 1%, whereas a more even distribution can be found in oil recovery from surfactant imbibition. Nevertheless, it seems that the range from 30 to 70% has relatively more frequency in limestone and dolomite.

Tertiary phase. Opposite to secondary phase, most imbibition tests in tertiary phase are implemented with dolomite. The number of imbibition tests in dolomite and limestone are 92 and 23, respectively. As shown in Fig. 16a, oil recovery from water imbibition covers 0–34.2%, with 4.5% on average. The range from 0 to 1% has the most frequency in dolomite and limestone. Oil recovery higher than 13.5% is detected as special cases from boxplots. As indicated by Standnes and Austad, the abnormal value can be partly related with moldic pore structure of carbonates, inhomogeneous wetting state at the outermost layer of the core, and thermal expansion of fluid [64,67]. Fig. 16b illustrates the incremental oil recovery by surfactant imbibition. It depicts that surfactant imbibition is capable to increase oil recovery by 1.1–92.9%, and 27.7% on average. Furthermore, big difference is found between limestone and dolomite. For limestone, more imbibition tests fall into the range from 40 to 70%. For dolomite, the range between 0 exclusive and 40% accounts for 80% of imbibition tests. To find the reason for such weak response from dolomite, the data source is carefully examined. It is documented that nearly 70% of dolomite data in the range from 0 exclusive to 40% is collected from the same institution [24,70]. The dolomite materials are collected from Cottonwood Creek field (Wyoming), Dagger Draw field (New Mexico), and Fuhrman-Masho field C zone (Texas). Aside from that, oil recovery from a fraction of cores is not increased. Such materials include dolomite from Fuhrman-Masho field B zone (Texas) and limestone from Eagle Creek field (New Mexico). As stated by Weiss and Xie, two factors possibly resulted in this ineffectiveness [24]. One is low permeability, and the other one is high amount of surfactant loss caused by adsorption on rock surface. Thus, permeability and rock mineralogy are suggested as significant factors for the design of surfactant huff-puff treatments. However, three samples with incremental oil recovery higher than 90% are dolomite cores with high permeability (101–352 mD) from West Texas. Fig. 16c depicts ultimate oil recovery which is defined as the sum of oil recovery from water imbibition and incremental oil recovery in this paper. Due to the oil recovery from water imbibition is often low, ultimate oil recovery presents a similar distribution with incremental oil recovery. The ranges with more frequency in limestone and dolomite are 40–70% and from 0 exclusive to 40%, respectively. The average of ultimate oil recovery is 32.2%.

The performance of oil recovery is summarized in Table 5. Given a certain rock type, comparison of oil recovery between secondary phase

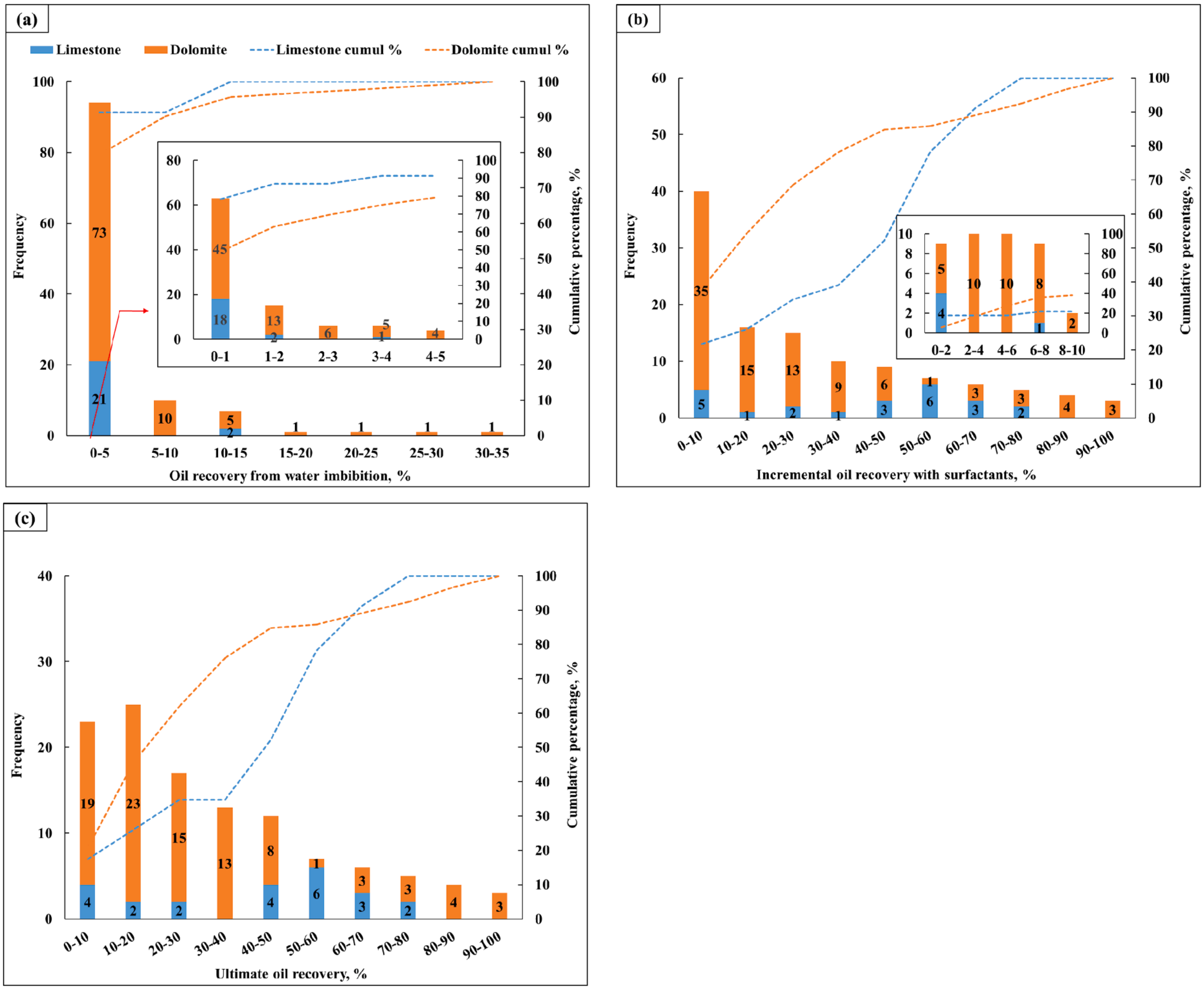

Fig. 16. Distribution of (a) oil recovery from water imbibition, (b) incremental oil recovery with surfactants, and (c) ultimate oil recovery.

Table 5
Summary of oil recovery in terms of rock types and recovery phases.

Rock types	Recovery phases	Count	Oil recovery from water imbibition, %	Count	Oil recovery from surfactant imbibition, %	Count	Ultimate oil recovery, %
Limestone	Secondary	27	0–6.9–20.3	161	1.2–38.3–91.1	–	–
	Tertiary	23	0–1.3–13.8	23	1.3–39.2–71.6	23	1.79–40.5–71.6
Dolomite	Secondary	1	14–14–14	40	6.3–44.8–80	–	–
	Tertiary	92	0–3.3–34.8	92	1.1–25.8–92.9	92	1.5–29.0–92.9
Overall	Secondary	28	0–7.1–20.3	201	1.2–39.1–91.1	–	–
	Tertiary	115	0–4.5–34.8	115	1.1–27.7–92.9	115	1.5–32.2–92.9

Note:
Range is presented with minimum - mean - maximum

and tertiary phase could assist in studying the effect of treatment timing on oil recovery performance. For limestone, the average oil recovery from tertiary phase is slightly higher than those from secondary phase. For dolomite, an opposite trend is observed. In addition, the difference of average oil recovery between two recovery phases is much larger than the difference in limestone. In general, the secondary phase is more favorable to produce oil from surfactant huff-puff treatments. The treatment timing is suggested to be taken into consideration for the design of surfactant huff-puff treatments.

7. Conclusions

In this study, a comprehensive dataset for wettability alteration with surfactants in carbonate rocks is constructed, which contains 338 effective surfactant imbibition tests published from 1996 to 2020. Ununiform data and duplicate data are eliminated to provide a high-quality dataset. Descriptive statistical analysis methods are used to conduct data analysis, and the following conclusions can be drawn:

- The application guidelines for surfactant huff-puff treatments in carbonate reservoirs are established. The guidelines indicate that surfactants can be effectively applied in wide ranges: porosity from 3.1 to 51.7%, permeability from 0.04 to 1458 mD, starting oil saturation from 37.7 to 100%, temperature from 20 to 100 °C, average contact angle from 55 to 180°, oil gravity from 22 to 75.2 °API, oil viscosity from 0.3 to 23 cp, acid number from 0 to 4.5 mg KOH/g oil, base number from 0 to 1.83 mg KOH/g oil, asphaltene concentration from 0 to 10.7 wt%, salinity of connate water and imbibition water from 0 to 263.7 g/l, divalent cations concentration of connate water and imbibition water from 0 to 24.6 g/l.
- Anionic, cationic, and nonionic surfactants are applied in 83% of imbibition tests, and cationic surfactants have the most frequency. The application ranges for these three types of surfactants are summarized: salinity of imbibition water (anionic 0–106 g/l, cationic 0–100 g/l, nonionic 0–263.7 g/l); salinity of connate water (anionic 0–118.1 g/l, cationic 0–213.7 g/l, nonionic 0–263.7 g/l); divalent cations concentration of imbibition water (anionic 0–4.4 g/l, cationic 0–4.4 g/l, nonionic 0–24.6 g/l); divalent cations concentration of connate water (anionic 0–6.2 g/l, cationic 0–21.5 g/l, nonionic 0–24.6 g/l); temperature is in the range 20–100 °C for three types of surfactants.
- A critical surfactant concentration higher than CMC is reported to exist where surfactants could achieve the best performance. Surfactant concentration is recommended to be kept near or higher than this critical concentration. Data analysis results show that surfactant concentration ranges from 0.01 to 5.0 wt%, where 97% of tests are conducted with concentration$<$2.0 wt%. Besides that, the range$<$1.0 wt% is observed as the peak range, which accounts for 75% of tests.
- Mixture of various surfactants and approximate usage of additives are useful strategies, which could improve surfactant solutions properties, extend applicable conditions, and enhance the effectiveness of surfactants.
- Surfactant solutions have been prepared from deionized water, formation water, produced water, seawater, and synthetic water. About 94% of surfactant solutions are prepared from synthetic water, which is composed of synthetic formation water, synthetic produced water, synthetic seawater, and electrolytes solution. Among them, synthetic formation water has the most frequency.
- Surfactant huff-puff treatments can be conducted either in secondary phase or tertiary phase. The range of oil recovery from secondary phase and tertiary phase are similar, which covers from 1.0 to 93%. While the average oil recovery from secondary phase and tertiary phase are 39.1% and 32.2%, respectively. Therefore, the treatment timing is suggested to be considered in the design of treatments.

CRediT authorship contribution statement

Ya Yao: Methodology, Writing - original draft. **Mingzhen Wei:** Supervision. **Baojun Bai:** Writing - review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

References

[1] Treiber LE, Archer DL, Owens WW. A laboratory evaluation of the wettability of fifty oil-producing reservoirs. SPE J 1972;12:531–40. https://doi.org/10.2118/3526-pa.

[2] Chilingar GV, Yen TF. Some notes on wettability and relative permeabilities of carbonate reservoir rocks II. Energy Sources 1983;7(1):67–75.

[3] Høgnesen EJ, Strand S, Austad T. Waterflooding of preferential oil-wet carbonates: oil recovery related to reservoir temperature and brine composition. SPE Eur. Annu. Conf. 2005. https://doi.org/10.2523/94166-ms.

[4] Alammari FG, Miller CS, Mohanty KK. Wettability altering surfactants for high temperature tight carbonate reservoirs. SPE Symp Improv Oil Recover 2020. https://doi.org/10.2118/200348-ms.

[5] Chen P, Mohanty KK. Surfactant-mediated spontaneous imbibition in carbonate rocks at harsh reservoir conditions. SPE J 2013;18:124–33. doi:10.2118/153960-PA.

[6] Graham JW, Mc Cardell WM, Richardson JG, Osoba JS. Method of increasing oil production. U.S. Patent No. 2,792,894., 1957.

[7] Craig MD. Oil recovery process employing cyclic wettability alteration. U.S. Patent No. 4842065, 1988.

[8] Chen HL, Lucas LR, Nogaret LAD, Yang HD, Kenyon DE. Laboratory monitoring of surfactant imbibition using computerized tomography. SPE Int Pet Conf Exhib 2000. https://doi.org/10.2118/59006-ms.

[9] Weiss WW, Xie X, Weiss J, Subramanium V, Taylor A, Edens F. Artificial intelligence used to evaluate 23 single-well surfactant soak treatments. SPE Reserv Eval Eng 2006;9:209–16. https://doi.org/10.2523/89457-ms.

[10] Zubari HK, Babu Sivakumar VC. Single well tests to determine the efficiency of Alkaline-Surfactant injection in a highly oil-wet limestone reservoir. SPE 13th Middle East Oil Show Conf.. 2003.

[11] Rilian NA, Sumestry M, Wahyuningsih. Surfactant stimulation to increase reserves in carbonate reservoir: "A case study in Semoga field". In: SPE Eur. Annu. Conf. Exhib.; 2010. https://doi.org/10.2523/130060-ms.

[12] Varfolomeev MA, Ziniukov RA, Yuan C, Khairtdinov RK, Sitnov SA, Sudakov VA, et al. Optimization of carbonate heavy oil reservoir development using surfactant flooding: from laboratory screening to pilot test. SPE Russ Pet Technol Conf 2020. https://doi.org/10.2118/201905-ms.

[13] Al-Sinani IS, Al-Jabri SH, Al-Rawahy NA, Al-Rawahy I, Al-Hinai K, Leksono M. Modified surfactant injection to enhance oil production and recovery, case study:

Omani carbonate reservoir. In: SPE EOR Conf. Oil Gas West Asia; 2016. https://doi.org/10.2118/179851-ms.

[14] Shuler PJ, Lu Z, Ma Q, Tang Y. Surfactant huff-n-puff application potentials for unconventional reservoirs. SPE Improv Oil Recover Conf 2016. https://doi.org/10.2118/179667-ms.

[15] Yao Ya, Wei Mingzhen, Kang Wanli. A review of wettability alteration using surfactants in carbonate reservoirs. Adv Colloid Interface Sci 2021;294:102477. https://doi.org/10.1016/j.cis.2021.102477.

[16] Kathel P, Mohanty KK. Dynamic surfactant-aided imbibition in fractured oil-wet carbonates. J Pet Sci Eng 2018;170:898–910. https://doi.org/10.1016/j.petrol.2018.06.088.

[17] Taber JJ, Martin FD. Technical screening guides for the enhanced recovery of oil. In: SPE Annu. Tech. Conf. Exhib.; 1983. https://doi.org/10.2523/12069-ms.

[18] Taber JJ, Martin FD, Seright RS. EOR screening criteria revisited - part 1: introduction to screening criteria and enhanced recovery field projects. SPE Reserv Eng 1997;12:189–97. https://doi.org/10.2118/35385-pa.

[19] Zhang N, Yin M, Wei M, Bai B. Identification of CO2 sequestration opportunities: CO2 miscible flooding guidelines. Fuel 2019;241:459–67. https://doi.org/10.1016/j.fuel.2018.12.072.

[20] Zhang Na, Wei Mingzhen, Fan Jiayi, Aldhaheri Munqith, Zhang Yandong, Bai Baojun. Development of a hybrid scoring system for EOR screening by combining conventional screening guidelines and random forest algorithm. Fuel 2019;256:115915. https://doi.org/10.1016/j.fuel.2019.115915.

[21] Zhang N, Wei M, Bai B. Statistical and analytical review of worldwide CO2 immiscible field applications. Fuel 2018;220:89–100. https://doi.org/10.1016/j.fuel.2018.01.140.

[22] Saleh LD, Wei M, Zhang Y, Bai B. Data analysis for polymer flooding that is based on a comprehensive database. SPE Reserv Eval Eng 2017;20:876–93. https://doi.org/10.2118/169093-pa.

[23] Qiu Y, Wei M, Bai B, Mao C. Data analysis and application guidelines for the microgel field applications. Fuel 2017;210:557–68. https://doi.org/10.1016/j.fuel.2017.08.094.

[24] Weiss WW, Xie X. Oilfield surfactants improve recovery by imbibition. SPE Int Symp Oilf Chem 2007. https://doi.org/10.2523/106402-ms.

[25] Bailey RE, Curtis LB. Enhanced Oil Recovery - National Petroleum Council. Washington, D.C.: 1984.

[26] Goodlett GO, Honarpour MM, Chung FT, Sarathi PS. Role of screening and laboratory flow studies in EOR process evaluation. In: SPE Rocky Mt. Reg. Meet.; 1986. https://doi.org/10.2118/15172-ms.

[27] Taber JJ, Martin FD, Seright RS. EOR screening criteria revisited - part 2: applications and impact of oil prices. SPE Reserv Eng 1997;12:199–204. https://doi.org/10.2118/39234-pa.

[28] Al-Bahar MA, Merrilll R, Peake W, Jumaa M, Oskui R. Evaluation of IOR potential within Kuwait. In: 11th Abu Dhabi Int Pet. Exhib. Conf.; 2004. https://doi.org/10.2523/88716-ms.

[29] Al Adasani Ahmad, Bai Baojun. Analysis of EOR projects and updated screening criteria. J Pet Sci Eng 2011;79(1-2):10–24. https://doi.org/10.1016/j.petrol.2011.07.005.

[30] Sheng James J. Status of surfactant EOR technology. Petroleum 2015;1(2):97–105. https://doi.org/10.1016/j.petlm.2015.07.003.

[31] Valluri MK, Cain R, Lalgudi R. Novel eco-friendly cationic surfactant for improving oil recovery from carbonate reservoirs. SPE Asia Pacific Oil Gas Conf Exhib 2018. https://doi.org/10.2118/191947-ms.

[32] Pola J, Geiger S, Mackay E, Bentley M, Maier C, Al-Rudaini A. The impact of micro- and meso-scale heterogeneities on surfactant flooding in carbonate reservoirs. In: SPE Eur. Featur. 81st EAGE Conf. Exhib.; 2019. https://doi.org/10.2118/195557-ms.

[33] Dong H, Yafei AA. Optimization of surfactant flooding for carbonate reservoirs. In: Abu Dhabi Int. Pet. Exhib. Conf.; 2015. https://doi.org/10.2118/177489-ms.

[34] Ghosh B, Obassi D. Eco-friendly surfactant for EOR in high temperature, high salinity carbonate reservoir. SPE Enhanc Oil Recover Conf 2013. https://doi.org/10.2118/165219-ms.

[35] Sagi AR, Puerto M, Bian Y, Miller CA, Hirasaki GJ, Salehi M, et al. Laboratory studies for surfactant flood in low-temperature, low-salinity fractured carbonate reservoir. SPE Int Symp Oilf Chem 2013. https://doi.org/10.2118/164062-ms.

[36] Berry SL, Smith K, Cutler JL, Kalfayan L. Improved oil recovery from combining well stimulation with novel surfactant technologies. SPE Annu Tech Conf Exhib 2009. https://doi.org/10.2118/124215-ms.

[37] Tabary R, Fornari A, Bazin B, Bourbiaux B, Dalmazzone C. Improved oil recovery with chemicals in carbonate formations. SPE Int. Symp. Oilf. Chem., 2009. doi:10.2118/121668-MS.

[38] Rostami Ravari Reza, Strand Skule, Austad Tor. Combined surfactant-enhanced gravity drainage (SEGD) of oil and the wettability alteration in carbonates: the effect of rock permeability and interfacial tension (IFT). Energy Fuels 2011;25(5):2083–8. https://doi.org/10.1021/ef200085t.

[39] Leslie Zhang D, Liu Shunhua, Puerto Maura, Miller Clarence A, Hirasaki George J. Wettability alteration and spontaneous imbibition in oil-wet carbonate formations. J Pet Sci Eng 2006;52(1-4):213–26. https://doi.org/10.1016/j.petrol.2006.03.009.

[40] Hirasaki GJ, Zhang DL. Surface chemistry of oil recovery from fractured, oil-wet, carbonate formations. SPE J 2004;9:151–62. https://doi.org/10.2118/88365-PA.

[41] Seethepalli A, Adibhatla B, Mohanty KK. Physicochemical interactions during surfactant flooding of fractured carbonate reservoirs. SPE J 2004;9:411–8. https://doi.org/10.2523/89423-ms.

[42] Adibhatla B, Mohanty K. Oil recovery from fractured carbonates by surfactant-aided gravity drainage: laboratory experiments and mechanistic simulations. SPE Reserv Eval Eng 2008;11:119–30. https://doi.org/10.2118/99773-pa.

[43] Gupta R, Adibhatla B, Mohanty KK. Parametric study to enhance oil recovery rate from fractured oil-wet carbonate reservoirs. SPE Annu Tech Conf Exhib 2008. https://doi.org/10.2118/116485-ms.

[44] Milter J, Austad T. Chemical flooding of oil reservoirs 6. Evaluation of the mechanism for oil expulsion by spontaneous imbibition of brine with and without surfactant in water-wet, low-permeable, chalk material. Colloids Surfaces A Physicochem Eng Asp 1996;113:269–78. doi:10.1016/0927-7757(96)03631-X.

[45] Gupta R, Mohan K, Mohanty KK. Surfactant screening for wettability alteration in oil-wet fractured carbonates. SPE Annu Tech Conf Exhib 2009. https://doi.org/10.2118/124822-ms.

[46] Gupta R, Mohanty KK. Temperature effects on surfactant-aided imbibition into fractured carbonates. SPE J 2010;15:587–97. https://doi.org/10.2118/110204-pa.

[47] Gupta R, Mohanty KK. Wettability alteration mechanism for oil recovery from fractured carbonate rocks. Transp Porous Media 2011;87(2):635–52. https://doi.org/10.1007/s11242-010-9706-5.

[48] Lu Jun, Goudarzi Ali, Chen Peila, Kim Do Hoon, Delshad Mojdeh, Mohanty Kishore K, et al. Enhanced oil recovery from high-temperature, high-salinity naturally fractured carbonate reservoirs by surfactant flood. J Pet Sci Eng 2014;124:122–31. https://doi.org/10.1016/j.petrol.2014.10.016.

[49] Sharma G, Mohanty KK. Wettability alteration in high-temperature and high-salinity carbonate reservoirs. SPE J 2013;18:646–55. https://doi.org/10.2118/147306-PA.

[50] Chen P, Mohanty KK. Wettability alteration in high temperature carbonate reservoirs. SPE Improv Oil Recover Symp 2014. https://doi.org/10.2118/169125-ms.

[51] Standnes Dag C, Austad Tor. Wettability alteration in carbonates: low-cost ammonium surfactants based on bio-derivatives from the coconut palm as active chemicals to change the wettability form oil-wet to water-wet conditions. Colloids Surf A Physicochem Eng Asp 2003;218(1-3):161–73. https://doi.org/10.1016/S0927-7757(02)00581-2.

[52] Chen P, Mohanty KK. Surfactant-enhanced oil recovery from fractured oil-wet carbonates: effects of low IFT and wettability alteration. SPE Int Symp Oilf Chem 2015. https://doi.org/10.2118/173797-ms.

[53] Han M, Fuseni AB, Yousef AA, Kokal SL, Al-Saleh S. Effect of surfactants on water imbibition into heterogeneous carbonate rocks at an elevated temperature. SPE Middle East Oil Gas Show Conf 2011. https://doi.org/10.2118/141205-ms.

[54] Qi Z, Han M, Fuseni A, Alsofi A, Zhang F, Peng Y, et al. Laboratory study on surfactant induced spontaneous imbibition for carbonate reservoir. SPE Asia Pacific Oil Gas Conf Exhib 2016. https://doi.org/10.2118/182322-ms.

[55] Chen P. Surfactant-enhanced spontaneous imbibition process in highly fractured carbonate reservoirs. The University of Texas at Austin; 2011.

[56] Austad T, Matre B, Milter J, Sævareid A, Øyno L. Chemical flooding of oil reservoirs 8. Spontaneous oil expulsion from oil- and water-wet low permeable chalk material by imbibition of aqueous surfactant solutions. Colloids Surf A Physicochem Eng Asp 1998;137(1-3):117–29. https://doi.org/10.1016/S0927-7757(97)00378-6.

[57] Chen P. Enhanced oil recovery in fractured vuggy carbonates. The University of Texas at Austin; 2014.

[58] Standnes DC. Enhanced oil recovery from oil-wet carbonate rock by spontaneous imbibition of aqueous surfactant solutions. Norwegian University of Science and Technology; 2001.

[59] Morrow NR, Buckley J. Wettability and oil recovery by imbibition and viscous displacement from fractured and heterogeneous carbonates. 2006.

[60] Gupta R. Surfactant treatment of oil-wet fractured carbonate reservoirs. University of Houston; 2009.

[61] Lu J. Development of novel surfactants and surfactant methods for chemical enhanced oil recovery. The University of Texas at Austin; 2014.

[62] Standnes Dag C, Austad Tor. Wettability alteration in carbonates: Interaction between cationic surfactant and carboxylates as a key factor in wettability alteration from oil-wet to water-wet conditions. Colloids Surf A Physicochem Eng Asp 2003;216(1-3):243–59. https://doi.org/10.1016/S0927-7757(02)00580-0.

[63] Austad T, Milter J. Spontaneous imbibition of water into low permeable chalk at different wettabilities using surfactants. Int. Symp. Oilf. Chem., 1997. doi:10.2118/37236-MS.

[64] Standnes Dag C, Austad Tor. Wettability alteration in chalk 1. Preparation of core material and oil properties. J Pet Sci Eng 2000;28(3):111–21. https://doi.org/10.1016/S0920-4105(00)00083-8.

[65] Standnes Dag C, Austad Tor. Wettability alteration in chalk 2. Mechanism for wettability alteration from oil-wet to water-wet using surfactants. J Pet Sci Eng 2000;28(3):123–43. https://doi.org/10.1016/S0920-4105(00)00084-X.

[66] Standnes Dag C, Nogaret Leslie AD, Chen Hung-Lung, Austad Tor. An evaluation of spontaneous imbibition of water into oil-wet carbonate reservoir cores using a nonionic and a cationic surfactant. Energy Fuels 2002;16(6):1557–64. https://doi.org/10.1021/ef0201127.

[67] Standnes Dag C, Austad Tor. Nontoxic low-cost amines as wettability alteration chemicals in carbonates. J Pet Sci Eng 2003;39(3-4):431–46. https://doi.org/10.1016/S0920-4105(03)00081-0.

[68] Strand S, Standnes DC, Austad T. Spontaneous imbibition of aqueous surfactant solutions into neutral to oil-wet carbonate cores: effects of brine salinity and composition. Energy Fuels 2003;17:1133–44. https://doi.org/10.1021/ef030051s.

[69] Goudarzi A, Delshad M, Mohanty KK, Sepehrnoori K. Impact of matrix block size on oil recovery response using surfactants in fractured carbonates. In SPE Annu. Tech. Conf. Exhib., 2012. doi:10.2118/160219-MS.

[70] Xie X, Weiss WW, Tong Z, Morrow NR. Improved oil recovery from carbonate reservoirs by chemical stimulation. SPE J 2005;10:276–85. https://doi.org/10.2118/89424-ms.

[71] Pinto MF. Wettability alteration in carbonates by surfactants: the effects of interfacial tension on this process and reflex in porous media behavior. Offshore Technol Conf 2013. https://doi.org/10.4043/24470-ms.

[72] Wu Y, Shuler PJ, Blanco M, Tang Y, Goddard WA. An experimental study of wetting behavior and surfactant EOR in carbonates with model compounds. SPE J 2008;13:26–34. https://doi.org/10.2118/99612-PA.

[73] Qiu Y, Wei M, Bai B. Descriptive statistical analysis for the PPG field applications in China: screening guidelines, design considerations, and performances. J Pet Sci Eng 2017;153:1–11. https://doi.org/10.1016/j.petrol.2017.03.030.

[74] Bohnsack D, Potten M, Pfrang D, Wolpert P, Zosseder K. Porosity–permeability relationship derived from Upper Jurassic carbonate rock cores to assess the regional hydraulic matrix properties of the Malm reservoir in the South German Molasse Basin. Geotherm Energy 2020;8:1–47. https://doi.org/10.1186/s40517-020-00166-9.

[75] HE Ling, ZHAO Lun, LI Jianxin, MA Ji, LUI Ruilin, Wang Shuqin, et al. Complex relationship between porosity and permeability of carbonate reservoirs and its controlling factors: a case study of platform facies in Pre-Caspian Basin. Pet Explor Dev 2014;41(2):225–34. https://doi.org/10.1016/S1876-3804(14)60026-4.

[76] Rashid F, Glover PWJ, Lorinczi P, Collier R, Lawrence J. Porosity and permeability of tight carbonate reservoir rocks in the north of Iraq. J Pet Sci Eng 2015;133:147–61. https://doi.org/10.1016/j.petrol.2015.05.009.

[77] Sun H. Data analysis of surfactant-induced wettability alteration in carbonate reservoirs. Missouri University of Science and Technology; 2016.

[78] Bera Achinta, S Kissmathulla, Ojha Keka, Kumar T, Mandal Ajay. Mechanistic study of wettability alteration of quartz surface induced by nonionic surfactants and interaction between crude oil and quartz in the presence of sodium chloride salt. Energy Fuels 2012;26(6):3634–43. https://doi.org/10.1021/ef300472k.

[79] Pal Sreela, Mushtaq M, Banat Fawzi, Al Sumaiti Ali M. Review of surfactant-assisted chemical enhanced oil recovery for carbonate reservoirs: challenges and future perspectives. Pet Sci 2018;15(1):77–102. https://doi.org/10.1007/s12182-017-0198-6.

[80] Austad T, Strand S, Høgnesen EJ, Zhang P. Seawater as IOR fluid in fractured chalk. In SPE Int. Symp. Oilf. Chem. 2-4 February, Woodlands, Texas, 2005. doi:10.2118/93000-MS.

[81] Austad Tor, Standnes Dag C. Spontaneous imbibition of water into oil-wet carbonates. J Pet Sci Eng 2003;39(3-4):363–76. https://doi.org/10.1016/S0920-4105(03)00075-5.

[82] Zhang P, Austad T. The relative effects of acid number and temperature on chalk wettability. In SPE Int. Symp. Oilf. Chem. 2-4 February, Woodlands, Texas, 2005. doi:10.2523/92999-ms.

[83] Xie Quan, He Shunli, Pu Wanfeng. The effects of temperature and acid number of crude oil on the wettability of acid volcanic reservoir rock from the Hailar Oilfield. Pet Sci 2010;7(1):93–9. https://doi.org/10.1007/s12182-010-0011-2.

[84] Puntervold T, Strand S, Austad T. Water flooding of carbonate reservoirs: effects of a model base and natural crude oil bases on chalk wettability. Energy Fuels 2007;21:1606–16. https://doi.org/10.1021/ef060624b.

[85] Buckley JS, Liu Y, Monsterleet S. Mechanisms of wetting alteration by crude Oils. SPE J 1998;3:54–61. https://doi.org/10.2118/37230-PA.

[86] Akhlaq Mohammed Shahid, Kessel Dagobert, Dornow Wolfgang. Separation and chemical characterization of wetting crude oil compounds. J Colloid Interface Sci 1996;180(2):309–14. https://doi.org/10.1006/jcis.1996.0308.

[87] Kovscek AR, Wong H, Radke CJ. A pore-level scenario for the development of mixed wettability in oil reservoirs. AIChE J 1993;39(6):1072–85. https://doi.org/10.1002/aic.690390616.

[88] Salehi Mehdi, Johnson Stephen J, Liang Jenn-Tai. Mechanistic study of wettability alteration using surfactants with applications in naturally fractured reservoirs. Langmuir 2008;24(24):14099–107. https://doi.org/10.1021/la802464u.

[89] Meyer RF, Attanasi ED, Freeman PA. Heavy oil and natural bitumen-strategic petroleum resources in geological basins of the world. vol. 1084. 2007.

[90] Kubelka Jan, Bai Shixun, Piri Mohammad. Effects of surfactant charge and molecular structure on wettability alteration of calcite: insights from molecular dynamics simulations. J Phys Chem B 2021;125(4):1293–305. https://doi.org/10.1021/acs.jpcb.0c10361.

[91] Maneedaeng Atthaphon, Flood Adrian E. Synergisms in binary mixtures of anionic and pH-insensitive zwitterionic surfactants and their precipitation behavior with calcium ions. J Surfactants Deterg 2017;20(1):263–75. https://doi.org/10.1007/s11743-016-1902-z.

[92] Julius P, Ananthanarayanan PN, Mohanakumar D. Alteration of wettability by cationic gemini and conventional surfactants for carbonate reservoirs. Indian J Sci Technol 2015;8:9–12. doi:10.17485/ijst/2015/v8i11/70681.

[93] Gao B, Sharma MM. A new family of anionic surfactants for enhanced-oil-recovery applications. SPE J 2013;18:829–40.

[94] Pal N, Saxena N, Mandal A. Studies on the physicochemical properties of synthesized tailor-made gemini surfactants for application in enhanced oil recovery. J Mol Liq 2018;258:211–24. https://doi.org/10.1016/j.molliq.2018.03.037.

[95] Kamal MS. A review of gemini surfactants: potential application in enhanced oil recovery. J Surfactants Deterg 2016;19:223–36. https://doi.org/10.1007/s11743-015-1776-5.

[96] Liu S, Zhang D, Yan W, Puerto M, Hirasaki GJ, Miller CA. Favorable attributes alkaline-surfactant-polymer flooding. SPE J 2008;13:5–16. https://doi.org/10.2118/99744-PA.

[97] Maerker JM, Gale WW. Surfactant flood process design for Loudon. SPE Reserv Eng 1992;7:36–44. https://doi.org/10.2118/20218-PA.

[98] Bera Achinta, Mandal Ajay. Microemulsions: a novel approach to enhanced oil recovery: a review. J Pet Explor Prod Technol 2015;5(3):255–68. https://doi.org/10.1007/s13202-014-0139-5.

[99] Ghosh P, Mohanty KK. Novel application of cationic surfactants for foams with wettability alteration in oil-wet low-permeability carbonate rocks. SPE J 2018;23:2218–31. https://doi.org/10.2118/179598-PA.

[100] Kalam Shams, Abu-Khamsin Sidqi A, Kamal Muhammad Shahzad, Patil Shirish. A review on surfactant retention on rocks: mechanisms, measurements, and influencing factors. Fuel 2021;293:120459. https://doi.org/10.1016/j.fuel.2021.120459.

[101] Pal N, Saxena N, Divya Laxmi KV, Mandal A. Interfacial behaviour, wettability alteration and emulsification characteristics of a novel surfactant: implications for enhanced oil recovery. Chem Eng Sci 2018;187:200–12. https://doi.org/10.1016/j.ces.2018.04.062.

[102] Kumar S, Mandal A. Studies on interfacial behavior and wettability change phenomena by ionic and nonionic surfactants in presence of alkalis and salt for enhanced oil recovery. Appl Surf Sci 2016;372:42–51. https://doi.org/10.1016/j.apsusc.2016.03.024.

[103] Zhang Peimao, Tweheyo Medad T, Austad Tor. Wettability alteration and improved oil recovery by spontaneous imbibition of seawater into chalk: Impact of the potential determining ions Ca2+, Mg2+, and SO42-. Colloids Surf A Physicochem Eng Asp 2007;301(1-3):199–208. https://doi.org/10.1016/j.colsurfa.2006.12.058.

[104] Shirazi Mahsa, Farzaneh Javad, Kord Shahin, Tamsilian Yousef. Smart water spontaneous imbibition into oil-wet carbonate reservoir cores: symbiotic and individual behavior of potential determining ions. J Mol Liq 2020;299:112102. https://doi.org/10.1016/j.molliq.2019.112102.

[105] Montazeri M, Fazelabdolabadi B, Shahrabadi A, Nouralishahi A, HallajiSani A, Moosavian SMA. An experimental investigation of smart-water wettability alteration in carbonate rocks–oil recovery and temperature effects. Energy Sources, Part A Recover Util Environ Eff 2020;1–13. https://doi.org/10.1080/15567036.2020.1759735.

[106] Karimi M, Al-Maamari RS, Ayatollahi S, Mehranbod N. Mechanistic study of wettability alteration of oil-wet calcite: the effect of magnesium ions in the presence and absence of cationic surfactant. Colloids Surf A Physicochem Eng Asp 2015;482:403–15. https://doi.org/10.1016/j.colsurfa.2015.07.001.

[107] Adegbite JO, Al-Shalabi EW, Ghosh B. Geochemical modeling of engineered water injection effect on oil recovery from carbonate cores. J Pet Sci Eng 2018;170:696–711. https://doi.org/10.1016/j.petrol.2018.06.079.

[108] Montazeri M, Shahrabadi A, Nouralishahi A, Mousavian SM, Sani AH. Investigation of wettability alteration due to smart water injection into carbonate reservoirs by zeta potential and contact angle ' s tests. Pet Res 2018;28:1–4. https://doi.org/10.22078/pr.2018.2475.2146.

[109] Mofrad SK, Saeedi Dehaghani AH. An experimental investigation into enhancing oil recovery using smart water combined with anionic and cationic surfactants in carbonate reservoir. Energy Rep 2020;6:543–9. https://doi.org/10.1016/j.egyr.2020.02.034.

[110] Deng Xiao, Tariq Zeeshan, Murtaza Mobeen, Patil Shirish, Mahmoud Mohamed, Kamal Muhammad Shahzad. Relative contribution of wettability alteration and interfacial tension reduction in EOR: a critical review. J Mol Liq 2021;325:115175. https://doi.org/10.1016/j.molliq.2020.115175.

[111] Schechter DS, Zhou D, Orr FM. Low IFT drainage and imbibition. J Pet Sci Eng 1994;11(4):283–300. https://doi.org/10.1016/0920-4105(94)90047-7.