Impact of Asphaltene Precipitation and Deposition on Wettability and Permeability

Isah Mohammed, Mohamed Mahmoud,* Ammar El-Husseiny, Dhafer Al Shehri, Karem Al-Garadi, Muhammad Shahzad Kamal, and Olalekan Saheed Alade

ABSTRACT: Asphaltene precipitation and deposition have been a formation damage problem for decades, with the most devastating effects being wettability alteration and permeability impairment. To this effect, a critical look into the laboratory studies and models developed to quantify/predict permeability and wettability alterations are reviewed, stating their assumptions and limitations. For wettability alterations, the mechanism is predominantly surface adsorption, which is controlled by the asphaltene contacting minerals as they control the surface chemistry, charge, and electrochemical interactions. The most promising wettability alteration evaluation techniques are nuclear magnetic resonance, ζ potential, and the use of high-resolution microscopy. The integration of such techniques, which is still missing, would reinforce the understanding of asphaltene interaction with rock minerals (especially clays), which holds the key to developing a strategy for modeling wettability alteration. With regard to permeability impairment, surface deposition, pore plugging, and fine migration have been identified as the dominant mechanisms with several models reporting the simultaneous existence of multiple mechanisms. Existing experimental findings showed that asphaltene deposition is non-uniform due to mineral distribution which further complicates the modeling process. It also remains a challenge to separate changes due to adsorption (wettability changes) from those due to pore size reduction (permeability impairment).

1.0. INTRODUCTION

Asphaltene deposition has profound consequences on the reservoir, tubings, and surface facilities. However, of pertinent interest is its implications in the reservoir where its impact can significantly affect productivity. The implication of the asphaltene problem results from the adsorption of asphaltene on the pore surface and the blockage of the flow path due to precipitation of asphaltene. This results in permeability reductions and alteration of the wettability state of the rock. Models have been developed to simulate formation damage due to precipitation, fine particle migration, dissolution/precipitation, and clay swell by history matching the model predictions to a laboratory core data test value. Observation showed that the solid depositions did not only affect permeability but also porosity as in the case of clay swelling. Thus, to investigate this concept, researchers have used different rock samples with different particle sizes in static and dynamic asphaltene adsorption experiments. This is in a bid to quantify and correlate the relationship, if there exists one, between mineralogy, particle sizes, and rate of deposition. Studies of the effect of adsorbent size (nano and micro), temperature, and pressure reveal a linear relationship between the temperature and rate of asphaltene desorption for the nanosized adsorbent. More so, irreversible adsorption was observed for the kaolin surface, which poses the question of reversibility of deposition on different surfaces.

Many models have been proposed to account for the different mechanisms of asphaltene deposition, each with its peculiarity and pitfalls. Thus, it is difficult to establish an all-fit-all model to account for the dynamics of asphaltene permeability impairment. Due to the many limitations of existing permeability impairment models, the gradual surface adsorption and pore blockage models to account for the permeability reduction in sandstone were developed. Comparisons of results from these models to the true permeability, as well as Wang and Civan’s model, reveal disagreements. Such deviations are attributed to the non-uniform adsorption of asphaltene and the inability of the models to honor heterogeneity. Nevertheless, several studies expressed optimism in the development of a correlation to

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relate temperature and mechanism dependent parameters with a physical process such as asphaltene deposition.

Experimental data and procedures have shown that the highlights of asphaltene deposition are pronounced in cumulative oil production. This can be attributed to the change in the relative permeability and instability of the brine film on the rock due to fluid interactions. Asphaltene interactions via molecular dynamics (MD) simulations show that asphaltene polar functional groups are responsible for hydrogen bond (HB) formation with fluid/rock systems, leading to alterations in the state of the rock. Meanwhile, the topology of the asphaltene molecule is said to affect the aggregation of molecules and that asphaltene interactions are not only dependent on the presence of heteroatoms and the type of asphaltene but also on the arrangements of the heteroatoms on the molecules.4

Several opinions regarding mechanisms of asphaltene deposition exist among researchers. So, this mini-review presents developments in permeability impairment modeling and wettability alteration quantification as well as a holistic view into the interaction between asphaltene and rock minerals. This is to provide insights into an area that is critical to the understanding and development of a robust control strategy to monitoring and combating asphaltene problems. Furthermore, this work seeks to identify gaps in the literature with regard to petrophysical implications of asphaltene deposition in the reservoir. First, wettability alteration is introduced along with the mechanisms and factors that affect reservoir rock wettability. This includes the effect of rock surface chemistry and asphaltene molecule interactions as well as the effects of pH, contacting minerals, and brine composition. After that, existing methods for wettability quantification are reviewed, with emphasis on the most recent developments, especially in the use of nuclear magnetic resonance (NMR) technique and \( \zeta \) potential measurement. Next, both experimental and modeling studies on permeability impairment are reported, highlighting limitations and potential further development. Lastly, some conclusions are drawn from the studies and summarized in the last section.

2.0. WETTABILITY ALTERATION

Reservoir wettability is an important concept in reservoir engineering and has been a subject of many studies over the years due to the enormous implication it has on production capacity. Wettability alteration has been largely attributed to changes in the pore system (adsorption), which may be due to rock–fluid interaction, fluid–fluid interactions, rock mineralogy, and brine chemistry. At the reservoir scale, a reservoir can be compartmentalized due to asphaltene, while at the pore scale asphaltene can create barriers to flow, change relative permeability and wettability of the rock, and, consequently, impact ultimate recovery. Asphaltenes mostly precipitate on rock surfaces non-uniformly, depending on the pore shape, surface roughness, and mineralogy. These may lead to either complete or partial changes in the wettability of the rock. The wettability of a reservoir is a result of a strong interfacial boundary condition that exists within the rock system which makes a fluid preferentially mobile in the presence of other fluids. Thus, it is predominantly due to the adherence or coating of the pore structure with a fluid that is either hydrophobic or hydrophilic. However, the adsorption of fluids onto the rock is affected by several factors, well operations, and interactions.

Fluid adsorption has gained popularity, especially in fluid transport in porous media and has drawn publications from both academia and industry to understand and quantify its effect in reservoir fluid production. Many articles exist on surfactant adsorption, polymer adsorption, gas adsorption, and nanoparticles but of interest to our review is the effect of asphaltene molecule adsorption. Asphaltene is said to be the most polar and heaviest component of crude oil, and its potential to adsorb on the pore walls has been reported.5

Asphaltene adsorbs on the pore surface, coating the surface and changing the wettability due to electrochemical interactions.6 Polar components in crude oil are said to be the most susceptible to adsorption. More so, the rate of adsorption by the polar compounds is linearly related to the wettability alteration. Contrary opinion to the relationship between crude oil, asphaltene composition, and adsorption has been expressed. This may be because the effect of rock–fluid interaction as well as brine was not captured in the model. Also, on the basis of asphaltene adsorption on carbonate rocks using isothermal titration calorimetry, NMR spectroscopy, and infrared spectroscopy, irreversibly adsorbed asphaltene has been reported.7 Furthermore, the literature has well documented, the factors that affect asphaltene adsorption onto rocks to include rock surface chemistry (charge and composition) and surrounding fluid property (pH, brine, and oil composition). Thus, the next section explores how each factor affects and contributes to asphaltene adsorption.

2.1. Factors That Affect Asphaltene Molecule Adsorption. 2.1.1. Surface Chemistry and Charge. Different minerals constitute rock samples and have a consequent effect on rock–fluid interaction. Constituent minerals and clays in reservoir rocks include calcite, dolomite, pyrite, kaolinite, chlorite, magnetite, hematite, illite, montmorillonite, quartz, and feldspar, etc. These minerals and clays possess surface charges and control the interactions with fluid systems. Surface charges of these minerals can also be altered by interactions such as an ionic exchange, adsorption, and deposition. For example, calcite, which is usually positively charged, can be made negative using sodium carbonate. Given this, the interaction between asphaltene molecules, ions, surfaces, and the reversal of charges is critical. The effect of rock–fluid interaction in sandstone and carbonate formations is well documented, but limited work has been done on the effect of contacting minerals and their surface charge on asphaltene destabilization. In our view, the most important factor is not the rock bulk mineralogy itself but the contacting minerals and their surface charge. This we believe holds the key to understanding the governing mechanism of asphaltene precipitation and deposition. This is so because the different rock types (minerals and clays) have different surface chemistry, charge types, and interactions with solvents, which is also a function of the medium pH.

Rock minerals and asphaltene molecules have an inherent net surface charge, and the two interacting molecules must possess opposite charges to cause wettability alteration. Although the net surface charge of rock minerals is well documented in the literature,8 the net surface charge of asphaltene molecules has been a subject of debate among researchers. The asphaltene molecules have been reported to possess a positive charge,9 while others5,10,11 have reported otherwise.

Recently, to resolve the debate on asphaltene net charge in different mediums, asphaltene electrokinetic properties were
studied using the electrophoresis technique.\textsuperscript{12} Asphaltene—
heptane, asphaltene—toluene, and asphaltene—heptol-50 mixtures were used for the experiments, with the asphaltene—toluene mixture serving as a replica of the conventional crude oil. Findings showed that the asphaltene—heptane mixture after application of the electric field had particles that were negatively charged. On the other hand, in the case of an asphaltene—toluene mixture, the movement of the aggregates was observed to be due to the monolayer of aggregates attached to the metallic surfaces causing the other aggregates to remain in solution. The behavior of the asphaltene—heptol-50 mixture was like the asphaltene—toluene mixture; however, the size of the aggregates was larger, thus the conclusion that the asphaltene molecule possesses a negative surface charge. In the same vein, the electrokinetic properties of asphaltene in static and dynamic conditions reveal its negative charge bearing property.\textsuperscript{13}

2.1.2. Medium pH. The pH of a medium measures how acidic or basic an environment is, and it is important in asphaltene science as many rock minerals develop surface properties that are dependent on medium pH which is also controlled by fluid composition. This thus contributes to the dynamics of rock—fluid interaction. The effect of brine composition, pH, and ionic strength on the electrokinetic charges of rock minerals can be ascertained by measuring the particle \( \zeta \) potential and electrophoretic mobility. This reveals in some cases charge reversal at high-pH values for mineral samples in the presence of divalent cations, thus signifying a high influence of the pH on formation rock surface charge. The effect of the presence of clay minerals and the use of synthetic brine was also studied; however, the effect of contacting minerals on the net surface charge is not considered. This is important because the most critical factor in chemical adsorption is not the rock mineralogy but the contacting mineral content.

Generally, to study the effect of pH on surface chemistry and ionic interactions, buffer solutions have been used to maintain the pH over a long time. Most researchers use HCl and NaOH solutions for their buffers of which X-ray diffraction (XRD) analysis and surface adsorption measurements have shown that exposure of minerals to acid and alkali treatments affect surface characteristics of the minerals. Several operations in the life of a well or reservoir affect the medium pH including treatment after drilling operation (pH < 4), low-salinity water-flooding (pH = 6–7), and alkaline flooding (pH > 10). These operations alter the rock surface and, thus, initiate rock—fluid interactions that otherwise were not possible. These, in turn, promote asphaltene molecule precipitation and consequently adsorption onto the surface. Different types of acid are used including mineral acids (HCl and HF), organic acids (formic acids and acetic acids), and retarded acids (gelled acids and emulsified acids), which have unique attributes and conditions for use in rock dynamics. Some of the possible chemical reactions between these treatment fluids are depicted in Table 1 and, as is vivid, results in the dissolution of potential determining ions from the minerals.

2.1.3. Oil/Brine Composition. Oil composition (polar compounds), as well as ions present in reservoir brine, have a significant effect on asphaltene precipitation and deposition which consequently results in wettability alteration. This is evident in the effect of sodium, calcium, and aluminum chloride based brines on asphaltene adsorption. Ultraviolet absorbance measurement of effluent concentration and spontaneous imbibition tests of Wyoming ‘95 and Prudhoe bay ‘95 crude oil samples reveal a high dependence on cationic valency of the brine and show an increase in asphaltene adsorption in the order Na\textsuperscript{+}, Ca\textsuperscript{2+}, and Al\textsuperscript{3+} for the same molar concentrations, due to ionic binding formation by the cations.\textsuperscript{15} Furthermore, a comparison of adsorbed asphaltene from both crude oils showed significant dependence of adsorption on the crude source as the Wyoming crude recorded higher adsorption result of asphaltene. Also, the dependency of imbibition rates and rock wettability on pore geometry and textural properties result in rapid adsorption in the first few pore volumes of injection of asphaltene solution. On the other hand, anions show little effect on wettability changes, however in decreasing effect order of NaCl, Na\textsubscript{2}CO\textsubscript{3}, Na\textsubscript{3}CO\textsubscript{3}, and Na\textsubscript{2}SO\textsubscript{4}.

An indirect method of analysis reveals the effect of iron-containing minerals on asphaltene stability. Thus, their influence is in the order Fe(III), Cr(III), Al(III), and Fe(II) and has more impact than the medium pH. However, chelating agents such as ethylenediaminetetraacetic acid (EDTA) proved to be successful in the presence of Fe(III), which does not prevent asphaltene precipitation or deposition. Similarly, diethylenetriaminepentaaetic acid (DTPA) can change the rock surface charge by stripping the rock of its cations. These anions increase recovery and prevent organic scales as in the case of asphaltene. Steric acid is used to modify rock surfaces to mimic the adsorption of a hydrophobic fluid. \( \zeta \) potential measurement and effluent ion concentration analysis reveal the mechanism of enhanced oil recovery (EOR) using seawater and low-salinity water. The exploration of the effect of brine chemistry holds the key to recovery as in low-salinity water-flooding. This is because different mineral surfaces have different interactions with fluids owing to their structure, charge, amount, and distribution within the pore structure. Furthermore, the recovery from low-salinity water (LSW) is

| Table 1. Chemical Reactions in Acid Treatment\textsuperscript{14} |
|---------------------------------------------------------------|
| montmorillonite (bentonite)-HF/HCl                             |
| kaolinite-HF/HCl                                               |
| albite-HF/HCl                                                  |
| orthoclase-HF/HCl                                              |
| quartz-HF/HCl                                                  |
| calcite-HCl                                                   |
| dolomite-HCl                                                  |
| siderite-HCl                                                  |

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\[ \text{montmorillonite (bentonite)-HF/HCl} \]

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\[ \text{albite-HF/HCl} \]

\[ \text{orthoclase-HF/HCl} \]

\[ \text{quartz-HF/HCl} \]

\[ \text{calcite-HCl} \]

\[ \text{dolomite-HCl} \]

\[ \text{siderite-HCl} \]

\[ \text{Al}_4\text{Si}_{10}\text{O}_{26} (\text{OH})_4 + 40\text{HF} + 4\text{H}^+ \rightarrow 4\text{AlF}_4^{2-} + 8\text{SiF}_4 + 24\text{H}_2\text{O} \]

\[ \text{Al}_4\text{Si}_{10}\text{O}_{26} (\text{OH})_4 + 40\text{HF} + 4\text{H}^+ \rightarrow 4\text{AlF}_4^{2-} + 8\text{SiF}_4 + 18\text{H}_2\text{O} \]

\[ \text{Na}_2\text{Al}_2\text{Si}_4\text{O}_{10} + 14\text{HF} + 2\text{H}^+ \rightarrow \text{Na}^+ + 2\text{AlF}_4^{2-} + 3\text{SiF}_4 + 8\text{H}_2\text{O} \]

\[ \text{KAl}_2\text{Si}_4\text{O}_{10} + 14\text{HF} + 2\text{H}^+ \rightarrow \text{K}^+ + 2\text{AlF}_4^{2-} + 3\text{SiF}_4 + 8\text{H}_2\text{O} \]

\[ \text{SiO}_2 + 4\text{HF} \rightarrow \text{SiF}_4 + 2\text{H}_2\text{O} + \text{SiF}_4 + 2\text{H}^+ \rightarrow \text{H}_2\text{SiF}_6 \]

\[ \text{CaCO}_3 + 2\text{HCl} \rightarrow \text{CaCl}_2 + \text{CO}_2 + \text{H}_2\text{O} \]

\[ \text{CaMg(CO}_3)_2 + 4\text{HCl} \rightarrow \text{CaCl}_2 + \text{MgCl}_2 + 2\text{CO}_2 + 2\text{H}_2\text{O} \]

\[ \text{FeCO}_3 + 2\text{HCl} \rightarrow \text{FeCl}_3 + \text{CO}_2 + \text{H}_2\text{O} \]
more sensitive to cation types rather than the salinity level of the medium and suggests the use of extended DLVO theory for candidate reservoir screening.\textsuperscript{16}

Investigation into the effect of injection fluid ionic content and pH on rock surface chemistry and wettability identified the dominant interaction forces to be van der Waals forces, hydrogen bonds, Coulomb forces, and surface forces.\textsuperscript{17} This further provided insight into the effect of rock surface chemistry and rock surface hydrophilicity as a function of environmental pH and laid the foundation for the understanding of the increased recovery observed in low-salinity flooding in carbonate and sandstone formations. Consequently, increasing the pH of the injected fluid in sandstone formation increases the surface hydrophilicity. On the other hand, high-salinity CaSO$_4$ and MgSO$_4$ brine enhance hydrophilicity in carbonates. Generally, the discussed factors affecting asphaltene adsorption are at interplay with each other which predicts asphaltene adsorption complex. Table 2 shows a summary of the factors as discussed in this section. More so, the effect of these factors may differ from reservoir to reservoir as well as in sandstone or carbonate formation.

### Table 2. Summary of the Effect of Factors Affecting Adsorption

| factor          | effect on adsorption                                                                 |
|-----------------|--------------------------------------------------------------------------------------|
| surface charge  | Surfaces with positive surface charges induces the adsorption of negatively charged polar crude oil constituents. Charge reversal is induced on some minerals and clays in the presence of cations. |
| pH              | Particle stability is reduced in an aqueous medium. Precipitation and ion dissolution are promoted. |
| oil composition | An increase in the saturate constituent of crude oil increases adsorption due to a decrease in asphaltene stability, which consequently wets the surface. |
| brine composition | The presence of cations and anions induces ionic interactions that promote adsorption; e.g., the presence of Mg$^{2+}$ and Ca$^{2+}$ changes the surface charge and results in adsorption of asphaltenes. |

2.2. Quantification of Wettability Alteration. Wettability quantification of a reservoir rock is essential as wettability controls productivity from the formation. Indexes are common ways of representing the wettability of a formation with the most used indexes being the U.S. Bureau of Mines (USBM) and Amott—Harvey (AH) index. These methods are time-consuming and, thus, limit their applicability for monitoring and understanding wettability alteration due to asphaltene adsorption and precipitation. Therefore, USBM and AH methods are not discussed here. Changes in wettability of a formation result from the coating of the surface by compounds or fluid—rock interactions and are often monitored especially in the enhanced oil recovery experimental process. Several techniques exist for the quantification of rock wettability, with each having its pros and cons. The knowledge about the change of wettability over time in a producing formation not only allows insight into future production capability but also allows the control of production dynamics to ensure a healthy state of the reservoir for optimum production. Presented next are insights gained from studies (experimental and modeling) carried out to quantify wettability alterations due to asphaltene deposition using innovative tools such as NMR analysis and $\zeta$ potential.

2.2.1. $\zeta$ Potential Measurement. In an ionic solution, particles that possess net charges move with definite velocity upon application of an electric field to the solution. This movement is termed electrophoretic mobility and is used to calculate $\zeta$ potential. Thus, $\zeta$ potential is the potential at the slipping plane of a particle in a medium and its measurement holds information such as the type and magnitude of surface charge on a suspended particle. It also informs about the stability and flocculation potential of a particle. Thus, it finds application in water treatment, flocculants development, and dispersants. More so, $\zeta$ potential values can indicate changes in the state of the surface such as wettability alterations. It is a qualitative technique that depicts a change in surface chemistry by reduction or increase in the magnitude and sign of the $\zeta$ potential value. But little or no correlation has been established with wettability other than a change in magnitude and sign of the $\zeta$ potential, which could be due to adsorption of fluids on the particle surface or dissolution of ions from the surface. Thus, at best it can only be used as a qualitative check.

Comparison of wettability alteration due to asphaltene using the $\zeta$ potential measurement and the popular Amott—Harvey and USBM methods is not straightforward and can be misleading. $\zeta$ potential as an indication of wettability alteration depends on the adsorbing fluid. More so, the effect of salts complicates the interpretation of $\zeta$ potential. However, it can quantitatively indicate a change in the state of the surfaces. Furthermore, the application of $\zeta$ potential measurement in wettability alteration studies availed the researchers the understanding of wettability changes but does not permit the observation of in situ alterations.

2.2.2. Nuclear Magnetic Resonance Technique. Nuclei with an odd number of neutrons or protons or both (i.e., hydrogen nucleus) possess a net magnetic moment and angular momentum (spin) such that measurable signals can be obtained when they interact with external magnetic fields. $^1$H NMR measurements are conducted by applying a static magnetic field (polarization process) on a given sample followed by a sequence of radio frequency (RF) pulses (excitation process). On the basis of the scheme of the excitation process, three main NMR parameters can be obtained, namely, longitudinal relaxation ($T_1$), transverse relaxation ($T_2$), and diffusion coefficient ($D$). Valuable rock and fluid properties obtained from these parameters, are pore size, permeability, and tortuosity, etc. Nuclear magnetic resonance has been recognized as one method for wettability evaluation due to its high sensitivity to the fluid—rock interaction strength. NMR techniques are non-intrusive and relatively fast compared to the conventional wettability evaluation methods such as USBM and Amott—Harvey. NMR $T_2$ relaxation time is a function of three mechanisms, bulk relaxation, surface relaxation, and diffusive relaxation, as presented in eq 1.

$$\frac{1}{T_2} = \frac{1}{T_{2,\text{bulk}}} + \frac{\rho_s}{V} A_s + D \left(\gamma G \tau_0\right)^2 \frac{12}{2}$$

where $\rho_s$ is the transverse surface relaxivity, $A_s / V$ is the pore surface area to volume ratio, $D$ is the fluid’s diffusion coefficient, $\gamma$ is the nuclei gyromagnetic ratio, $G$ is the magnetic field gradient, and $\tau_0$ is the time between 180° pulses in the Carr—Purcell—Meiboom—Gill (CPMG) sequence (echo time). The diffusive relaxation (third term on the right-hand side (RHS) of eq 1) can be neglected for fluid-saturated rocks when low magnetic field instruments and sufficiently short echo spacing are used. $T_1$ relaxation is a function of only bulk
Asphaltene adsorption can change the surface chemistry of the pores, resulting in a reduction of $T_2$ relaxation times as asphaltene can enhance the surface relaxation process. The impact of asphaltene adsorption on surface relaxivity is the basis for linking changes in $T_2$ relaxation times with wettability changes, because $T_2$ relaxation is enhanced when molecules contact (wet) the surface. However, other factors other than wettability changes such as water droplets accumulation can influence the $T_2$ values. A combination of low- and high-field NMR, in addition to other supporting measurements such as 3D microtomography, scanning electron microscopy (SEM), and electron paramagnetic resonance (EPR), etc., can foster the understanding of the relationship between asphaltene adsorption and deposition, aging process kinetics, and wettability alteration processes. NMR measurements of n-decane fully saturated cores before and after aging lead to the development of the wettability index used to quantify wettability. The wettability index of the rock is based on the observed surface relaxivity shown in eq 2.

$$I_{NMR}(t) = I_o - I_w = \frac{2(\rho_{ow} - \rho_w(t))}{\rho_{ow} - \rho_{ew}} - 1$$

(2)

where $\rho_w(t)$ is the surface relaxivity of the n-decane-saturated rock at a given aging time, $t$, $\rho_{ow}$ and $\rho_{ew}$ are the surface relaxivities of a strongly water-wet core ($S_w = 1$ and $I_{NMR} = 1$) and a strongly oil-wet core ($S_o = 1$ and $I_{NMR} = -1$), respectively. The conclusions are that the aging process can be classified into three phenomenologically different stages. In the first stage (5–7 days), a discontinuous asphaltene layer is formed, leading to relatively quick wettability alteration (wettability is reduced). The second stage (22–24 days) represents the optimum aging time where asphaltene micelle, consisting of aliphatic molecules, is formed, resulting in the greatest complete wettability change step. Finally (above 24 days), in the last stage, no more wettability change occurs but the surface relaxivity still significantly increases due to the intense development of aliphatic-rich macroaggregates, which alters rock morphology. Another important observation is that oil with the maximum asphaltene proportion shows the minimum asphaltene adsorption capacity due to the presence of a high resin fraction as in the case of heavy oils. Figure 1 shows the alteration of effective surface relaxivity over aging time for Bentheimer sandstone cores saturated with different oils, namely, OM.1 (1.57 wt % asphaltenes), OM.2 (2.81 wt % asphaltenes), and OM.3 (3.93 wt % asphaltenes). This work was conducted on clear-cut samples of simple mineralogy and morphology and saturated with one phase which is the model oil n-decane. However, the situation becomes more challenging for carbonate rocks of complex structure and morphology. Also, the presence of brine adds more complexity to wettability change dynamics. For instance, thick brine films that develop on the mineral surface could hinder asphaltene adsorption.

The above studies use $T_2$ measurements to qualitatively monitor wettability changes or estimate indices that can be linked to wettability changes. Nevertheless, the relationship between the index estimated for example using eq 2 and the conventional wettability index as measured by Amott–Harvey or USBM is not established. Since NMR $T_2$ relaxation is strongly related to fluid–rock interaction (eq 1) and thus wettability, several studies attempted to produce an NMR-derived wettability index whose magnitude can be comparable with those estimated from conventional Amott–Harvey or USBM. This is developed on the basis of the concept that the enhancement of surface relaxation of a fluid is proportional to the surface area coated by that fluid. The concept here is that the nonwetting phase shows only bulk relaxation, while the wetting phase experiences enhanced relaxation as it contacts more surfaces. In this case, the relaxation time of water for example will be shorter in the water-wet sample than that in the oil-wet sample. The index requires conducting relaxation measurements at four different saturation states (full water saturation, $S_{ow}$, $S_{or}$, and full oil saturation) as shown in eqs 3 and 4.

$$I_{NMR} = \frac{S_o(\frac{1}{T_2o} - \frac{1}{T_{2or}}) + C p S_w(\frac{1}{T_2w} - \frac{1}{T_{2ow}})}{S_w(\frac{1}{T_2w} - \frac{1}{T_{2ow}}) + C p S_o(\frac{1}{T_2o} - \frac{1}{T_{2or}})}$$

(3)

Figure 1. Surface relaxivity evolution of different aged rocks. Reprinted with permission from ref 18. Copyright 2019 American Chemical Society.

Table 3. Reservoir Lithology Relaxivity

| lithology | relaxivity (μm/s) |
|-----------|------------------|
| sandstone | 23               |
| dolomite  | 5                |
| limestone | 3                |
| shale     | 1.7              |

Table 4. Reservoir Fluids Relaxation Times

| fluid | bulk $T_2$ (s) |
|-------|----------------|
| oil   | 0.0001–6       |
| water | 3–4            |
| gas   | 1–5            |
Due to the need for conducting wettability index due to asphaltene adsorption. This is likely here that the NMR-derived wettability index from the above approaches and input parameters. It is worth mentioning No wettability alteration means that $S_w$ and $S_o$ respectively. The other NMR $T_2$ wettability indices are based on a similar idea but with different approaches and input parameters. The effect of CO$_2$ on wettability alterations due to asphaltene precipitation can also be observed via NMR $T_2$ relaxation measurements. In this case, the samples are fully saturated with brine ($S_w = 1$) and then crude oil is injected into the samples until connate water saturation ($S_w$) is reached. $T_2$ measurements are then conducted at the previous saturations. After that, CO$_2$ is injected into the samples until no oil is produced and the samples are cleaned with ether which does not dissolve asphaltene. Finally, the same process of core saturation and $T_2$ measurements is repeated after CO$_2$-flooding. For this process, the introduced wettability alteration index $(I_{WA})$ is as follows (eqs 5, 6, and 7).

$$C_o = \frac{1/T_{2w100} - 1/T_{2w}}{1/T_{2o100} - 1/T_{2o}}$$

(4)

where $T_{2w}$ and $T_{2o}$ are the dominant relaxation times of water and oil at residual oil and irreducible water saturation, respectively. $T_{2w100}$ and $T_{2o100}$ are the dominant relaxation times of bulk water and oil, respectively. $S_w$ and $S_o$ are the water and oil saturations corresponding to $T_{2w}$ and $T_{2o}$, respectively. $C_o$ is the surface relaxivity ratio of water to oil. $T_{2w100}$ and $T_{2o100}$ are the dominant relaxation times of water and oil at 100% water and oil saturation, respectively. The other NMR $T_2$ wettability indices are based on a similar idea but with different approaches and input parameters. It is worth mentioning here that the NMR-derived wettability index from the above approach was never utilized to calculate changes in the wettability index due to asphaltene adsorption. This is likely due to the need for conducting $T_2$ measurements at various saturation points which can be experimentally demanding, especially if various aging times are involved.

The effect of CO$_2$ on wettability alterations due to asphaltene precipitation can also be observed via NMR $T_2$ relaxation measurements. In this case, the samples are fully saturated with brine ($S_w = 1$) and then crude oil is injected into the samples until connate water saturation ($S_w$) is reached. $T_2$ measurements are then conducted at the previous saturations.

Furthermore, experimental evidence showed a decrease in wettability alteration involves many mechanisms which include asphaltene precipitation and rock surfaces, and the control of surface charges. Continuous asphaltene precipitation causes continuous wettability alteration as presented in the above model is not consistent with the results mentioned earlier, thus the use of ratios. $T_1/T_2$ ratio, obtained from 2D $(T_1-T_2)$ NMR measurements, has also been used for qualitative evaluation of wettability. When the motion of the molecules is fast and isotropic, such as in the bulk nonviscous fluid, the $T_1/T_2$ is equal to 1. However, $T_1/T_2$ becomes greater than 1 as the motion of molecules becomes slow (i.e., high viscous fluids or solids) or no anisotropic (i.e., wetting fluids). The $T_1/T_2$ ratio correlates well to the USBM wettability index. Besides, it was used as a better choice than $T_2$ when relaxation from diffusion (third term on the RHS of eq 1) is significant. However, a major limitation of this technique is that the $T_1/T_2$ ratio for oil especially containing asphaltene may deviate from unity affecting wettability interpretation.

### 2.2.3. Other Techniques

Numerical studies on formation-induced damage and wettability alteration due to asphaltene deposition using sets of nonlinear equations serve as an alternative technique. These describe the multiphase, convection—adsorption, and diffusion mechanism by employing the implicit pressure and explicit saturation (IMPES) nonlinear solution technique as well as the line successive over relation (LSOR) iterative techniques. Reduction in oil production, increase in watercut, and changes in the relative permeabilities are a consequence of wettability alteration. However, numerical model predictions are often not benchmarked against existing models to ascertain their reliability and efficiency.

The inverse gas chromatography (IGC) technique has led to the development of a wettability index based on the concept of the surface energies (i.e., adhesion forces) of rock and fluids. The starting point for this is the van Oss—Chaudhury—Good model, that describes the adhesion work ($W_{12}^A$) between two surfaces (1 and 2), which reflects the degree of attraction strength between two surfaces as in eq 8:

$$W_{12}^A = 2\sqrt{\gamma_{1W} \gamma_{2W} + 2\sqrt{\gamma_{1W} \gamma_{2W}^*} + 2\sqrt{\gamma_{1W}^* \gamma_{2W}^*}}$$

(8)

where $\gamma_{1W}$ and $\gamma_{2W}$ are Lifshitz—van der Waals surface energy components of surfaces 1 and 2, respectively. $\gamma_1$ and $\gamma_2$ are surface energy basic and acidic components, respectively. Similarly, they introduced the work of adhesion for a system of the three phases: rock (S), brine (W), and oil (O) as shown in eqs 9 and 10.

$$W_{WS}^A = 2\sqrt{\gamma_{WS} \gamma_{WS}^* + 2\sqrt{\gamma_{WS} \gamma_{WS}^*} + 2\sqrt{\gamma_{WS} \gamma_{WS}^*}}$$

(9)

$$W_{OS}^A = 2\sqrt{\gamma_{OS} \gamma_{OS}^* + 2\sqrt{\gamma_{OS} \gamma_{OS}^*} + 2\sqrt{\gamma_{OS} \gamma_{OS}^*}}$$

(10)

where the parameters in eqs 9 and 10 are calculated from the inverse gas chromatography technique or obtained from the literature. This introduced a dimensionless wettability index (eq 11) of the same range of conventional Amott—Harvey and USBM indices ($-1$ to 1).

$$WI = \frac{W_{WS}^A - W_{OS}^A}{W_{WS}^A + W_{OS}^A}$$

(11)

This approach found application especially in Saudi Arabia but, like others, is not benchmarked. Furthermore, this method requires conducting experiments on rock powder, which is not an actual representation of reservoir rocks. Finally, micro-CT imaging has been used for the evaluation of wettability through the estimation of contact angles of different fluids inside multiphase saturated core samples. However, these measurements are limited to mm size samples and are constrained to both processing issues and image resolution.

### 2.3. Wettability Alteration Control

A control strategy to wettability alteration involves many mechanisms which include the stability of water film coating the rock surface, reduction in electrochemical and interfacial interactions between asphaltene molecules and rock surfaces, and the control of surface charges of the rocks. More recently, the use of solvents that contain functionalized molecules that react with asphaltene at the molecular level has been explored using sophisticated tools. Furthermore, experimental evidence showed a decrease in aromaticity of asphaltene, viscosity reduction, and decrease in
asphaltene deposition due to solvent injection. So generally, wettability reversal is predominantly by ionic interaction, which involves the injection of fluid that would either react with asphaltene to form complexes that have less affinity for the reservoir rock or has more affinity and would dislodge asphaltene from the surface, thus promoting more water-wetness. Another approach involves exposure of asphaltene coated rocks to UV and microwaves. This technique is based on the radiation absorption capacity of the polar crude components, which results in selective heating of these components and the creation of hot zones that lead to the reduction in viscosity and subsequently wettability reversal. However, such a technique is limited to laboratory experiments and has no field application. Injection of engineered water or modification of production strategy has also been reported in the field scale to reduce asphaltene wettability damage, but this is a preventive rather than a corrective measure and has limited success as a corrective measure. This involves the injection of water stripped of cations or negatively impacting PDIs such as Mg$^{2+}$ and Ca$^{2+}$ that would result in the adsorption of asphaltene onto the rock surface. However, this would have a limited effect if adsorption has already begun; thus, it is a strategy that should be implemented at the early stages of production.

3.0. PERMEABILITY IMPAIRMENT

Asphaltene deposition has profound consequences on the reservoir, tubings, and surface facilities, but of pertinent interest in this section is the reservoir implications of permeability impairment. Field-scale modeling of permeability impairment revealed that permeability damage in fractures due to asphaltene depositions is more considerable compared to the matrix media. Experimental techniques, as well as modeling approaches, have been developed to quantify permeability impairment in reservoirs. The governing mechanism of permeability impairment has been recognized to include fine migration, surface deposition, pore-throat plugging, and reentrainment of solid into the liquid phase. A review of experimental and modeling studies is treated next to holistically present what is known and identify the gaps still open for further research.

3.1. Experimental Studies. Several researchers have used different rock samples with different particle sizes (nano to micro) in static and dynamic asphaltene adsorption experiments in a bid to quantify and correlate the relationship, if there exists one, between mineralogy, particle sizes, rate of deposition, and permeability impairment. Also, the effects of asphaltene precipitation on the hydraulic radius, effective porosity, and absolute and relative permeability of reservoirs to quantify its implications on flooding performance using a core flooding experimental setup have been evaluated. Most findings reveal a reduction in permeability, porosity, hydraulic radius, and high-water relative permeability curve, which is attributed to the crude oil high asphaltene content which resulted in higher irreducible water saturations and thus limited recovery from water-flood operations.

The alterations of permeability, porosity, and wettability due to asphaltene deposition in a miscible gas injection process in high-pressure, high-temperature experimental conditions have also been reported. Contrary to popular belief, a decrease in effluent fluid asphaltene content (from 6.56 to 3.69 wt % for limestone and from 6.56 to 4.11 wt % for sandstone) is attributed to adsorption and a later increase (up to 8.59 wt % for limestone and 7.11 wt % for sandstone) to desorption of adsorbed asphaltene. This implies that adsorption is reversible, which is contrary to popular belief of the irreversibility of adsorption, more so to account for permeability reduction arithmetic technique which involves subtracting the asphaltene content in the produced fluid from the initial is used. This negates the thought that the reduction may as well be due to pore plugging and entrapment of flocculated molecules. Permeability reduction, in many cases, is related to the mineralogy (iron content) of the samples, which leads to permeability damage. However, no quantitative correlation between the mineralogy, porosity, and permeability damage factors has been established. Thus, the reduction of the iron content of a rock sample (Fe$^{3+}$ and Fe$^{2+}$) reduces the affinity of polar compounds to the rock surface. More so, on the basis of the SARA analysis of the deposited residue, an increase in resin and asphaltene contents may be an indicative factor.

The use of a solid detection system has received good attention recently, as it can accurately detect asphaltene systems though with a drawback of not being able to differentiate between other solids and asphaltene. It has provided insight into the dominant asphaltene deposition mechanisms in porous media and its effect on permeability alteration as a function of crude viscosity. More so, findings from experimental studies show that the dominant mechanism of deposition is dependent on the cause of the asphaltene destabilization. More so, the impact of asphaltene deposition on permeability is more severe at the gas injection well.

The use of the $T_2$ NMR relaxation measurements to quantify the degree and effect of asphaltene precipitation on the microscopic pore-structure changes, mainly pore blockage, during CO$_2$-flooding in low-permeability sandstone rocks has been established. The measurements are performed at different conditions (immiscible, near-miscible, and miscible CO$_2$-flooding). The cleaned samples are fully saturated with formation water and displaced by distilled water of 15,000 mg/L Mn$^{3+}$ concentration to remove the formation water hydrogen signal. Then, crude oil containing asphaltene is injected into the samples until no water is produced to obtain initial oil saturation. $T_2$ measurement is conducted at the obtained initial oil saturation. After that, CO$_2$ is injected into the samples until residual oil saturation is reached and $T_2$ measurement is conducted. The samples are cleaned with toluene to remove the residual oil, and finally, the clean sample is dried to establish the initial oil saturation. The $T_2$ measurements are then used to estimate the reduction of pore size due to precipitation by comparing $T_2$ relaxation at the initial oil saturation before and after CO$_2$ injection. The assumption, in this case, is that the diffusion and bulk transverse relaxation in eq 1 can be neglected by making $T_2$ relaxation mainly a function of surface relaxation, so eq 3 becomes

$$\frac{1}{T_2} = \rho_2 \frac{A_2}{V} = \rho_2 \frac{F_i}{r}$$

(12)

where $r$ is the pore radius and $F_i$ is the pore-throat dimensionless shape factor. Rearranging eq 12 as follows,

$$r = CT_2$$

(13)

where $C = \rho_2 F_i$ is a constant called the converted coefficient factor and obtained by matching the $T_2$ pore size distribution with that produced from the mercury injection experiment. In
addition, quantitative estimation of blockage degree is achieved using eq 14 as follows:

$$B = \frac{S_{1t}}{S_{01} + S_{02}} \times 100$$  

(14)

where $B$ is the degree of blockage and $S_{1t}$ and $S_{02}$ represent the areas under the $T_2$ distribution measured at the initial oil saturation before and after CO$_2$-flooding, respectively. Conclusions are that increasing the injection pressure, increases the asphaltene precipitation where the most significant precipitation occurs at near-miscible conditions while a slight increase happens at miscible conditions. Moreover, the degree of blockage in the smaller pores is lower than that in the larger pores for injection pressures less than 10 MPa. However, for higher injection pressure (miscible conditions) the smaller pores show a greater blockage degree than the larger pores. One major limitation here is the assumption of constant surface relaxivity which is not true for most of the cases. Furthermore, when oil saturates the core, its composition will affect both the amplitude and the $T_2$ values, leading possibly to the wrong conclusion if interpreted as pore size.

Permeability restoration has been attempted both at the laboratory and field scales by the use of dispersants,\textsuperscript{21} chelating agent nanoparticles, laser technology, microwave, and ultra-violet light (UV). The use of laser technology for permeability impairment restoration due to asphaltene has highlighted the degree of permeability restoration dependent on the laser intensity, with the optimum exposure time of 1 h enough to recover the permeability. Earlier, a novel experimental technique of treating an asphaltene damaged core using steam soaking was demonstrated. The rationale behind such thought is the reduction in viscosity and surface energy responsible for the adsorption of asphaltene on the rock. However, the mechanism in which the steam injection would follow to improve the permeability is not established. More so, the cost effect and required quantity of steam to achieve these permeability restorations would be an economic concern. So conclusively, it can be said that even though the mechanisms of permeability impairment have been established in different studies, their dominance and conditions that inform which mechanisms are simultaneously acting is not established yet. Further studies can attempt to establish a relationship between the identified permeability impairment mechanism, rock types, fluid composition, and interactions.

3.2. Modeling Studies. Several models have been proposed to account for the different mechanisms of asphaltene deposition, and each with its peculiarity makes it difficult to establish an all-fit-all model to account for the dynamics of asphaltene permeability impairment. However, researchers have expressed optimism in the development of a correlation to relate permeability impairment, temperature, and mechanism dependent parameters. As early as 1997, models were developed to simulate formation damage due to asphaltene precipitation, fine particle migration, dissolution/precipitation, and clay swell by history matching the model predictions to a laboratory core data test value. Findings reveal that the solid depositions did affect not only permeability but also porosity as in the case of clay swelling, which has a high surface area to volume ratio, and as well as ion exchange within the porous media. The size of the particles of the porous media could also be an influencing factor given that different porous media minerals have different surface charges which could lead to adsorption of asphaltene to the surface.

An asphaltene prediction tool based on the solid phase flash calculations has also been developed using the Peng–Robinson equation of state for the solid–liquid and vapor–liquid equilibrium calculations. This, like other tools, is dependent on the quality of crude characterization and precipitation data which led to the adjustment of the bubble point pressure using the interaction parameters. As against chemical injection, a reversal in the direction of flow can restore damaged formation permeability as the most dominant mechanism is pore plugging. Similarly, the equation of state (EoS) compositional simulator of asphaltene precipitation and deposition by incorporating the plugging and adsorption mechanism into an equation of state has been used. In this approach, asphaltene is modeled as a pure solid, with the oil and gas modeled using an EoS with volume shift parameters. The model yielded a good representation of the asphaltene phase behavior data and revealed that precipitated asphaltene can deposit onto the rock; however, it does not quantify the effect of wettability and particle trapping on production. More so, its reliability is dependent on a good characterization scheme and the interaction coefficients between the hydrocarbon constituents. The interaction coefficient between hydrocarbons which is used to tune the model is given as in eq 15:

$$\delta_{ij} = 1 - \left( \frac{2v_{ij}^{1/6}}{v_{ci}^{1/3}v_{cj}^{1/3}} \right)^{2e}$$  

(15)

where $v_{ij}$ is the critical volume of components $i$ and $j$ and $e$ is an adjustable parameter. The adsorbed mass fraction ($w_{sa}$) is defined as in eq 16

$$w_{sa} = \frac{N_{as}M_s}{(1 - \phi)\rho_R}$$  

(16)

where $N_{as} =$ number of molecules adsorbed per grid block volume, $M_s$ = molecular weight of asphaltene component, $\theta =$ porosity, and $\rho_R =$ rock density. The plugging is modeled, according to eq 17, in terms of resistance factor which has a linear correlation with the maximum amount of asphaltene adsorption in the flow path, thus depicting a reduction in flow area due to flow path constriction.

$$R_f = 1 + \left( R_{f,max} - 1 \right) \frac{w_{s,i}}{w_{s,a,max}}$$  

(17)

In the above equation, $w_{s,a}$ is adsorbed mass fraction, $R_f =$ resistance factor, $R_{f,max}$ is the maximum resistance factor corresponding to maximum adsorption $w_{s,a,max}$.

Furthermore, algorithms for asphaltene permeability damage predictions using the multisolid thermodynamics approach by applying each component’s fugacity and phase properties at equilibrium also exist. Slim tube experiments along with the thermodynamic model are used to simulate the permeability reduction with good agreements achieved; however, this approach honors more the fluid–fluid interaction than the depositional mechanism governing impairments. In the same vein, the permeability impairment model based on gel particle concentration and permeability reduction at a constant rate (eq 18) has been demonstrated, but more recently, a report of lack of fit of the model highlights its drawbacks to include external mixing of the oil–solvent mixture owing to the ease of flocculation.
\[
\frac{K}{K_0} = 1 - a \left( \frac{E_a}{E_i + b} \right)
\]  
(18)

where \(a\) and \(b\) are empirical constants and \(E_a\) = volume fraction of deposited asphaltene.

Against the use of correlations, a unique way of assessing permeability impairments by dividing the cores into segments was developed. The divided cores are then analyzed for permeability impairment to highlight the fact that deposition is not uniform within the porous media as such an assumption of overall permeability reduction would be wrong. More so, a comparison of the experimental data and prediction, using cementation factors of 2, 3, and 5 showed a lack of fit due to the use of a linear correlation model. Even though the adopted technique addressed some experimental gaps ignored by previous researchers, it is not without its flaws. First, the overburden pressure effect was ignored due to the sand packs used. Second, the mechanism of asphaltene deposition in this approach did not address the question of what mechanism is responsible for permeability impairment even though the authors showed the irreversibility of asphaltene deposition. Modifications of the Wang and Civan model to assess asphaltene deposition and permeability impairment are looked at by authors to account for the plugging mechanism. The original Wang and Civan’s model is expressed as eq 19:

\[
-\nabla \left( \frac{R_{Aos}}{B_o} + \frac{C_A u_o}{B_A} \right) - \frac{C_A q_{opec}}{B_A} + \frac{R_A q_{opec}}{B_o} = \frac{\partial}{\partial t} \left( \frac{C_A \phi S_o}{B_o} + \frac{R_A \phi S_o}{B_o} + E_A \right)
\]

(19)

where \(R_{Aos}\) is the volume ratio of soluble asphaltene in oil, \(B_o\) is the oil formation volume factor, \(C_A\) is suspended asphaltene saturation, \(u_o\) is oil phase velocity, \(B_A\) is asphaltene formation volume factor, \(q_{opec}\) is the flow rate, \(S_o\) is oil phase saturation, \(\phi\) is porosity, and \(E_A\) is the volume fraction of deposited asphaltene. The modified model accounts for the pore-throat plugging by incorporating eq 20:

\[
\text{pore-throat plugging} = \gamma (1 + \alpha E_a) (u_o - V_{CT}) C_A
\]

(20)

where \(\gamma\) is the instantaneous plugging deposition rate coefficient, \(\alpha\) is the snowball effect deposition coefficient, and \(V_{CT}\) is the critical interstitial velocity for entrainment and is based on the modified expression. The resulting asphaltene deposition model is

\[
\frac{dE_A}{dt} = \alpha e^{-\frac{E_a}{RT}} C_A \phi - \beta e^{-\frac{E_a}{\phi}} \left( u_o - V_{CT} \right) + \gamma (1 + \alpha E_a) (u_o - V_{CT}) C_A
\]

(21)

where \(\alpha\) is the surface deposition rate coefficient. This model upon comparison with the original Wang and Civan’s model shows better agreement with the experimental data set owing to its ability to capture the governing permeability impairment mechanisms. Until now, no model has accounted for the time dependence of deposition. Thus, the time dependence of permeability impairments due to asphaltene based on two or three mechanisms that are acting simultaneously as an improvement to Al-Ibadi and Civan’s model is proposed. The mechanisms considered are pore surface deposition, plugging, cake formation, and asphaltene entrainment due to high velocity in a low-permeability reservoir. Different tests (three cores with different porosity and permeability) conducted one after the other (1, 2, and 3) resulted in different permeability reduction trends (Figure 2) depicting different mechanisms in the tests conducted. This was ascertained by modeling each mechanism separately using diagnostic equations and comparing their trends with the experimental results. Findings showed that experimental results fit more than one mechanism (as the three cores show different permeability reduction trends owing to different acting mechanisms), depicting the simultaneous existence of mechanisms. Furthermore, it was highlighted that in a low-permeability reservoir, an increase in asphaltene particle size due to aggregation results in higher permeability damage. On the other hand, a decrease in asphaltene particle size in the same reservoir with low asphaltene content increases the damage due to plugging by fine particles. Thus, for a low-permeability reservoir, the existence of either asphaltene aggregates or fine particles results in permeability damages.

Recently, an indication that permeability impairment models needed to account for the pore/hydraulic connectivity in addition to the asphaltene deposition to accurately represent permeability dynamics in the formation (see Figure 3) is of concern. Models developed on the basis of critical path analysis, which revealed the dominant mechanism in different formations, are explored. This in comparison to the earlier models which assumed the effect of surface deposition in low-permeability formation is negligible, explicitly demonstrating that surface deposition has a significant effect and should be accounted for in permeability impairment modeling. However, most models agreed on the magnitude of permeability reduction compared to porosity. Similarly, owing to the pitfall of the earlier models to describe the porosity—permeability reduction in the case of solvent injection and non-uniform pore size, a permeability-porosity relation accounting for the pore size distribution was developed by Ghadimi et al. The findings show that the pore plugging mechanism effect on permeability reduction is abrupt, whereas the surface deposition effect is gradual and shows convex (reduction in permeability progressively until flow reversal or increase in flow velocity) and concave (maximum surface coverage by molecules as described by adsorption isotherms) curves, respectively. This also further explains the reason why earlier models could not capture the surface deposition as the time required for its effect to be pronounced is in seconds. More so, when the time variable is not captured in the impairment...
4.0. IDENTIFIED GAP AND FUTURE WORK

A literature review on the petrophysical impact of asphaltene precipitation and deposition has revealed that the most dominant mechanism of wettability alteration is surface adsorption which is affected or controlled by several other factors such as brine/oil composition, rock chemistry, and rock–fluid interactions. However, existing models are all based on the assumption of homogeneous wettability in the formation. This assumption results in having a single wettability index value to represent the complex rock microstructure whose wettability may vary spatially. Thus, the development of a spatial wettability index is needed to effectively capture the dynamics of this phenomenon. More so, tools such as NMR show observed changes in $T_1$ or $T_2$ spectra are due to either precipitation, deposition, or adsorption. Nevertheless, it remains a challenge to separate changes due to adsorption for example (wettability changes) from those due to pore size reduction (permeability impairment). Further research needs to be conducted in this area to establish a mechanism-dependent spectra analysis technique that would aid the identification of mechanisms from the NMR signal, probably by integrating with other petrophysical measurements. Also, there exists no quantitative relationship between the $\zeta$ potential measurements reported and adsorption to explicitly evaluate wettability. However, there exists an opportunity to explore the $\zeta$ potential of different mineral surfaces and how their surface charge and interactions relate to adsorption which can be translated to wettability.

With regard to permeability impairment, surface deposition, pore plugging, and fine migration have been identified as the dominant mechanisms with several models reporting the simultaneous existence of more than one mechanism. Recently, efforts are being made to develop a multimechanistic model that captures the physics of the problem, but none has been successful in delineating the simultaneous mechanisms to identify which is dominant. Interestingly, no work in literature reports the effect of asphaltene precipitation and deposition on the electrical and acoustic properties of reservoir rocks. This is a virgin area of research that holds much promise. We believe that if there exists a relationship between the acoustic or electrical properties and surface wettability or pore plugging, sonic or electrical logging might provide useful insights about down-hole changes due to asphaltene deposition. Furthermore, to provide insight into how asphaltene precipitation and deposition result in formation damages, and wettability alterations, density functional theory as well as molecular dynamics simulations can be instrumental. These tools provide a molecular-scale understanding of the mechanisms in play and would serve as a critical tool to the development of a robust strategy. Also, in situ process imaging techniques such as microfluidic devices, Micro-CT, NMR, and MRI even though at a small scale, provide useful information about the processes at the pore level though it is difficult to tell what the dominant mechanism is from these techniques. However, they do hold promises of contributing to the development of a robust solution as research relating to these techniques especially the NMR is ongoing. Emerging techniques to probe asphaltene deposition such as the use of crustal microbalance, and atomic force microscopy is another are in their infant stage. These techniques however limited in use, provide useful information for asphaltene deposition analysis. Lastly, asphaltene science is a broad area with several interesting areas to explore especially with regard to its control and prevention. Fundamental understanding of the nature and interactions of asphaltene holds the key to the development of a robust strategy to address its growing concern which can only be addressed by interdisciplinary collaborations among researchers from academia and industry.

5.0. CONCLUSIONS

Reviewing the experimental studies and models on petrophysical implications of asphaltene precipitation and deposition provided insights into how far developments have come with regard to being able to predict the implications. The dominant mechanisms of permeability impairment are pore plugging and
surface deposition, whereas for wettability alterations, the predominant mechanism is surface adsorption which is affected by several factors such as brine/oil composition, rock chemistry, and rock–fluid interactions. Nevertheless, these mechanisms vary and may occur simultaneously in different formations, thus making it difficult to identify the dominant mechanisms. The most promising wettability alteration quantifying techniques are NMR, ζ potential, and the use of high-resolution microscopy techniques which would reinforce the understanding of the interactions between asphaltene and rock minerals as well as clays that hold the key to developing a strategy for modeling these impairments. Evident from the extensive review of the mechanisms and factors that control asphaltene adsorption and deposition, the most important factor is not the rock minerals but the asphaltene contacting minerals as it controls the interactions which could be due to surface chemistry, charge, and electrochemical interactions. More so, the presence of clay has a significant impact and the development of chelating agents and charge controlling chemicals may help control the interactions that lead to wettability alterations. This is thus an area that requires further exploration. Furthermore, the change of wettability in different pH mediums is yet unexplored and may provide insights into wettability changes in enhanced oil recovery. Existing permeability models except those based on NMR do not have the capability of inferring where the most damage occurred either in large, medium, or small pores. Thus, it is imperative to incorporate pore-throat size in permeability models as implemented by only a few. Also, existing experimental findings showed that asphaltene deposition is non-uniform due to rock composition (clays and minerals) which further complicates the modeling process. Lastly, scarce in literature is the effect of asphaltene deposition on the electrical and acoustic properties of the rock. This holds importance as asphaltene precipitation has been reported in the literature due to the streaming potential.

■ AUTHOR INFORMATION

Corresponding Author

Mohamed Mahmoud — Petroleum Engineering Department, College of Petroleum Engineering and Geosciences, King Fahd University of Petroleum and Minerals, Dhahran 31261, Kingdom of Saudi Arabia; orcid.org/0000-0002-4395-9567; Email: mmahmoud@kfupm.edu.sa

Authors

Isah Mohammed — Petroleum Engineering Department, College of Petroleum Engineering and Geosciences, King Fahd University of Petroleum and Minerals, Dhahran 31261, Kingdom of Saudi Arabia; orcid.org/0000-0002-3420-7910

Ammar El-Husseiny — Geosciences Department, College of Petroleum Engineering and Geosciences, King Fahd University of Petroleum and Minerals, Dhahran 31261, Kingdom of Saudi Arabia; orcid.org/0000-0001-5762-6109

Dhafer Al Shehri — Petroleum Engineering Department, College of Petroleum Engineering and Geosciences, King Fahd University of Petroleum and Minerals, Dhahran 31261, Kingdom of Saudi Arabia

Karem Al-Garadi — Petroleum Engineering Department, College of Petroleum Engineering and Geosciences, King Fahd University of Petroleum and Minerals, Dhahran 31261, Kingdom of Saudi Arabia

Muhammad Shahzad Kamal — Center for Integrative Petroleum Research (CIPR), College of Petroleum Engineering and Geosciences, King Fahd University of Petroleum and Minerals, Dhahran 31261, Kingdom of Saudi Arabia; orcid.org/0000-0003-2359-836X

Olaheadline Seheed Alade — Center for Integrative Petroleum Research (CIPR), College of Petroleum Engineering and Geosciences, King Fahd University of Petroleum and Minerals, Dhahran 31261, Kingdom of Saudi Arabia; orcid.org/0000-0002-1657-9737

Complete contact information is available at: https://pubs.acs.org/10.1021/acsomega.1c03198

Author Contributions

Conceptualization: M.M., D.A.S., and I.M. Methodology: A.E.-H., M.M., M.S.K., and I.M. Writing original draft preparation: I.M., K.A.-G., and O.S.A. Writing review and editing: A.E.-H., K.A.-G., I.M., M.M., M.S.K., and D.A.S. Supervision: A.E.-H., M.M., and O.S.A. All authors contributed to the writing, editing, and proofreading of the manuscript. All authors have read and agreed to the published version of the manuscript.

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Biographies

Isah Mohammed is a third-year Ph.D. student under the supervision of Dr. Dhafer Al Shehri and Professor Mahmoud Mohammed. His area of interest is in asphaltene precipitation and deposition with emphasis on rock fluid interactions. He received his M.Sc. in Petroleum Engineering from the African University of Science and Technology, Abuja, Nigeria.

Professor Mohamed Mahmoud received his Ph.D. in Petroleum Engineering from Texas A&M University in 2011. He has experience cutting across roles as an application scientist, petroleum engineer, and drilling engineer. His research interests vary and cover well stimulation, enhanced oil recovery, multiphase flows in horizontal and vertical wells, and flow assurance (asphaltene and wax).

Dr. Ammar El-Husseiny received his M.Sc. and Ph.D. in Geophysics from Stanford University, USA in 2013 and 2016, respectively. His area of interest is rock physics of carbonate, fluid substitution and time-lapse seismic interpretation, and the use of NMR for pore-structure characterization.

Dr. Dhafer Al Shehri received his Ph.D. in Petroleum Engineering from Texas A&M University in 1994 and an Executive MBA degree from King Fahd University of Petroleum and Minerals in 2014. He is an experienced academic and industry professional with 19 years of association with Saudi Aramco and 14 years with KFUPM. His research interest is in petroleum economics, reservoir engineering and management, and enhanced oil recovery.

Mr. Kareem Al-Garadi is a second-year Ph.D. student at the Department of Petroleum Engineering, KFUPM. He received his bachelor’s and master’s degrees in Petroleum Engineering from KFUPM. He is working as a Teaching Assistant at the Department of Petroleum Engineering, KFUPM. He received extensive training at The University of Western Australia (UWA) in advanced NMR rock core and fluids analysis techniques, specifically wettability measurements. His research interests include NMR application in petrophysics, especially wettability evaluation.
Dr. Muhammad Shahzad Kamal is a Research Engineer II at the Centre for Integrated Petroleum Research (CIPR), KFUPM. He received his Ph.D. in Chemical Engineering from KFUPM in 2014. His area of expertise includes rheology of complex fluids, chemical EOR, oilfield chemistry, and interfacial phenomena.

Dr. Olalekan Saheed Alade is a visiting Research Engineer III at the Centre for Integrated Petroleum Research (CIPR), KFUPM. He received his Ph.D. in Earth Resources Engineering from Kyushu University, Japan in 2017, with specialties in hydrocarbon resources production. His research experiences span thermal and nonthermal.

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