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Comparison of original and de-asphalted crude oils during formation of HCl-induced emulsion and sludge

Ahmad Abbasi ^a, M. Reza Malayeri ^{a,*}, Maysam Mohammadzadeh-Shirazi ^{b,c}^a Department of Chemical Engineering, School of Chemical and Petroleum Engineering, Shiraz University, Shiraz, 7134851154, Iran^b Department of Petroleum Engineering, School of Chemical and Petroleum Engineering, Shiraz University, Shiraz, 7134851154, Iran^c Formation Damage and Well Treatment Research Group, IOR/EOR Research Institute, Shiraz University, Shiraz, 7134851154, Iran

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ABSTRACT

Stable HCl-crude oil emulsion and its subsequent sludge formation, with detrimental impacts on oil production, may stem from acid stimulation. One major ambiguity in this process is to discern the most influential component of crude oil on the stability of formed emulsions. This fundamental question has not adequately been addressed in previous studies. In this work, the impact of de-asphalted part of crude oil (maltene) has been investigated on the acid-induced emulsion and sludge separately. Accordingly, the emulsion phase separation and the amount of formed sludge have been compared for four crude oils and their maltene samples for different concentrations of ferric ion and acidic pH values. The results of phase separation, as a criterion for emulsion stability, showed that crude oil samples formed 6 to 25 percent more stable emulsions than maltene samples, when using blank HCl. The emulsions of maltene and spent acid (pH = 2) broke completely during the first 15 min after emulsification. In addition, the maltene components usually had less contribution to sludge formation in the presence of blank HCl. It was concluded that asphaltene is the key component during interaction with HCl. However, the maltene of one crude sample formed higher acid sludge in comparison to its crude oil. For acid solutions containing 3000 ppm of ferric ion, the emulsion stability increased for all crude oil and maltene samples. Moreover, the stability of some maltene emulsions increased to 48% and 100% in the presence of 3000 ppm of ferric ions. The presence of ferric ions caused forming very stable emulsions, while most of the sludge formation took place at higher pH values. Finally, it was also attained that emulsion and sludge formations could happen simultaneously.

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1. Introduction

Stable emulsion and sludge formation may occur during acid stimulation of oil reservoirs. A stable emulsion is known as a system of two immiscible liquids, such as HCl solution droplets dispersed in a crude oil medium, which would not break for a certain period of time. In other words, sludge can be considered as a solid-like or viscous phase, a very concentrated slurry, or a tight emulsion that forms in various industries such as water treatment, and various soft deposits in oil production and refinery. Acid-induced sludge is known as an insoluble unwanted solid-like product during contact and reaction between acid and crude oil (Jacobs and Thorne, 1986;

Moore et al., 1965). It has been reported that sludge can even be formed during the exposure of an asphaltene-free crude oil with acid (Rietjens, 1997). It has also been experienced that heavy crude oils tend to form rigid film emulsion, while acid-induced sludge is formed from light crude oils (Houchin et al., 1990). It can therefore be said that acid-induced sludge is a result of chemical interactions between acid ions and polar components of crude oil. Thus, its nature seems different from other petroleum sludge, which may be known as tight, rigid film or stable acid-crude oil emulsion.

A strong HCl solution can neutralize the basic components of the crude oil (Wong et al., 1997). When this happens, then the charge equilibrium between asphaltene and resin, as a peptizing agent of asphaltene, would be diminished causing asphaltene molecules to form flocs and consequently a stable emulsion. Furthermore, more adsorption of reacted components on the acid droplets' surface results in the growth of flocs and compacting of the interfacial layer. Sludge is formed exactly at the interface of acid and crude oil

* Corresponding author.

E-mail address: malayeri@shirazu.ac.ir (M.R. Malayeri).

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(Mirkhoshhal et al., 2021). Under such circumstances, it is difficult to distinguish between emulsion and sludge. In other words, several researchers identified acid-induced sludge as a viscous emulsion that is stabilized by organics rich in asphaltene (Wong et al., 1997). Accordingly, for a typical crude oil, sludge is defined as a tight emulsion, which cannot pass through a 100-mesh (Pourakaberian et al., 2021).

Asphaltene is known as the key component of the crude oil in sludge formation. It is reported that acid cannot form sludge in crude oils without asphaltene (Asaadian et al., 2022). On the other hand, a study on acid-induced sludge characterization also showed that sludge was richer in polar components such as asphaltene and resin than the initial crude oil (Wong et al., 1997). Oxygenated compounds may have an important role in sludge formation. Studying the chemical composition of the acid-crude oil interface showed that resin was absent and asphaltene with a high amount of heteroatoms detected in the stabilizing layer (Ganeeva et al., 2020). This means that maltene components, especially resin, cannot participate in the stabilizing layer around the acid droplets. As a result, it cannot either stabilize acid-crude oil emulsion or form acid-induced sludge. In contrast, it has been reported that the de-asphalted part of crude oil (maltene) has a considerable role in acid-induced sludge formation and the structure of its reactive components makes a difference in the formed sludge amount (Mohammadzadeh-Shirazi et al., 2019). Based on the results of bottle tests for sludge evaluation due to the exposure of HCl with synthetic oils consisting of different saturates and solvents, it is understood that lower aromaticity of the synthetic oil and higher solvent polarity cause more asphaltic sludge formation (Kalhori et al., 2022). Moreover, pure aromatics and saturates cannot form sludge when mixed with HCl solutions.

Among various studies on the water in crude oil emulsions as a common phenomenon in the petroleum industry, resin is known as one of the primary components in forming stable emulsion along with asphaltene (Berridge et al., 1968). However, there is no consensus on the effect of de-asphalted components of crude oil, such as resin, on the stability of water-oil emulsion. In another study, maltene was added to a synthetic oil consisting of asphaltene in a toluene solution in order to study the stability of water in an oil emulsion (Poteau et al., 2005). The results showed that interactions between asphaltene and smaller amphiphilic molecules in the maltene such as naphthenic acids except resin, improve the emulsion stability. It has been shown that the stability of emulsions made by just maltene was very weak. Several other researchers believed that resin cannot stabilize water in crude oil emulsions in the absence of asphaltene (Ortega et al., 2010; Zaki et al., 2000). It has also been reported that after separating polar components from the crude oil with a silica column, the remaining organic phase was not able to form an emulsion with water (Ebeltoft et al., 1992; Sjöblom et al., 1990; Urdahl et al., 1992).

The stability of oil emulsions is generally affected by the pH of aqueous phase. Water separation in pH-adjusted aqueous-crude oil emulsions showed a reverse relation between pH (from 2 to 6) and the emulsion stability due to a weaker acidic (HCl) environment (Daaou and Bendedouch, 2012). On the other hand, forming very stable emulsions without any phase separation has been reported when a concentrated HCl solution (20 wt%) was mixed with two different crude oil samples in the absence of any chemical additives during the first 15-min period (Alhamad et al., 2023). In another study, the emulsion phase separation decreased sharply by concentrating the aqueous phase from distilled water to 15 and 28 wt% HCl solution, especially at the beginning (Abbasi and Malayeri, 2022).

Several studies also investigated the impact of operating conditions such as temperature, mixing shear, and volume fraction of

the liquid phases. For instance, the volume fraction of the aqueous phase has been identified as an important factor in emulsion formation, type, and stability, especially in the acidizing process. A direct relation between phase separation and the volume fraction of acid solution in the emulsion has been reported in several recent studies in the range of 0.16–0.84 (Abbasi et al., 2024b; Hedayati et al., 2023). In addition, a reduction in the phase separation of the HCl-crude oil emulsion was observed when the shear was increased from 500 to 12000 rpm during the emulsification process (Abbasi et al., 2024b; Hedayati et al., 2023).

Sludge formation depends on the type of crude oil. Previously, asphaltene to resin and saturate to aromatic ratio was used as a representative of crude oil type in a predictive model for evaluating the potential formation of sludge (Pourakaberian et al., 2021). Furthermore, ferric ion, as a consequence of corrosion in the injected acid, intensifies the amount of acid-induced sludge (Garrouch et al., 2006; Mirkhoshhal et al., 2021; Mohammadzadeh-Shirazi et al., 2019). In addition, ferric ion causes increasing in the emulsion stability of HCl-crude oil emulsion due to higher asphaltene precipitation (Al-Mubarak et al., 2015).

The above-discussed literature survey reveals that there are still ambiguities around the role of maltene in the stabilization of acid-crude oil emulsion and sludge formation. It is not clear that other components of crude oils except asphaltene may contribute to emulsion stability and acid-induced sludge. In addition, the potential of forming emulsion and sludge for the de-asphalted part of the crude oil is not well understood. Thus, in this study, a set of experiments has carefully been designed to investigate the impact of various maltene samples on emulsion and sludge formation followed by a comparison with crude oil samples. The results would help a better understanding of interactions between HCl and crude oil components based on the crude oil type, its properties, and components. Furthermore, such findings would help the production engineers to discern the most challenging components of the crude oil in sludge formation and hence the pertinent prevention techniques.

2. Methodology

2.1. Materials

Four crude oil samples (C1 to C4) have been used in this study of which their properties are summarized in Table 1, *n*-heptane with a minimum purity of 95% was used to separate asphaltene from maltene (M1 to M4) for each crude oil sample, as will be explained in the following section. Hydrochloric acid with a purity of 37 wt% was purchased from Dr. Mojallali Company. Deionized water was used for acid dilution and washing the formed sludge besides hot diesel. $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ powder with a purity of 98% (Kimia Exir Co.) as a source of ferric ions, and Whatman filter paper of grade 42 with a pore size of 2.5 μm was used for separating asphaltene from maltene. Stainless steel 100-mesh was used for separating the formed sludge from the emulsion and liquid phases.

2.2. Maltene preparation

Asphaltene was precipitated from crude oil samples according to the IP-143 standard method with some modifications to prepare maltene. A certain amount of each crude oil sample was mixed with pure *n*-heptane (1 g crude oil: 40 mL *n*-heptane). Then, the whole mixture was placed at rest in a dark container for 24 h to allow the precipitated asphaltene to settle down. To ensure complete precipitation of asphaltene, these two steps were repeated twice. Next, it was filtered using a vacuum pump to separate precipitated asphaltene from the liquid phase. After that, the trapped asphaltene

Table 1
Properties of crude oil samples and their maltene.

Crude oil	Density, g/cm ³	Saturate, wt%	Aromatic, wt%	Resin, wt%	Asphaltene, wt%	CII ^a
C1	0.930	43.4	35.6	12.9	8.1	1.06
C2	0.905	54.7	25.9	14.7	4.7	1.46
C3	0.933	52.8	31.7	9.7	5.8	1.42
C4	0.903	47.6	31.7	17.0	3.7	1.05
Maltene						
M1	0.923	47.2	38.7	14.1	0	0.89
M2	0.857	57.4	27.2	15.4	0	1.35
M3	0.900	56.1	33.7	10.2	0	1.28
M4	0.890	49.4	32.9	17.7	0	0.98

^a Colloidal instability index.

on the filter paper was washed with a reflux Soxhlet extractor setup containing pure *n*-heptane to remove paraffin-soluble material. This step continued until the refluxed *n*-heptane became clear. The contaminated *n*-heptane, which had wax, resin, and other components except asphaltene, was then added to the previous filtered solution and let it evaporate to make it free of its *n*-heptane in a large beaker at room temperature. The remaining liquid is the de-asphalted crude oil or maltene. The constant measured weight of the remained maltene in several days indicated that no more *n*-heptane was present in the evaporating container. For later analyses, the density of maltene samples was measured and the weight fractions of its components were calculated based on the SARA analysis of the crude oil samples, which are reported in Table 1. It is worth mentioning that the measured mass of the original oil was approximately equal to the sum of masses of the extracted asphaltene and the remained maltene for each of the samples, which confirmed negligible variation in the oil fractions after evaporation of *n*-heptane. On the other hand, only dead oil samples were used which were free of light fractions and some dissolved gases. Therefore, it can be said that there was no composition variation between crude oil and maltene, except the extracted asphaltene.

2.3. Test design

A set of experimental tests was designed to investigate the role of maltene on emulsion stability and acid-induced sludge formation as presented in Table 2. First, the reference tests were designed using a blank acid solution (15 wt% HCl) without any other additives, i.e. ferric ions. Then, the effect of ferric ions on emulsion and sludge formation was studied at a ferric ion concentration of 3000 ppm in the blank HCl solution. This concentration is reported to happen in wellbores as a result of corrosion caused by the injected acid (Coulter and Gougler, 1984). Finally, to simulate the spent acid condition, the effect of acid pH on emulsion stability and sludge formation was studied for both crude oil and maltene samples by diluting the blank acid solution with deionized water to obtain the pH of 2, which is common for the spent and even the

Table 2
Details of experiments.

Test	Organic phase	Aqueous phase	[Fe ³⁺], ppm	pH
Reference	Crude oil	15 wt% HCl	0	0
	Maltene	15 wt% HCl	0	0
Ferric ion	Crude oil	15 wt% HCl	3000	0
	Maltene	15 wt% HCl	3000	0
Higher pH	Crude oil	Diluted HCl	0	2
	Maltene	Diluted HCl	0	2

returned acid from the reservoir after neutralization to some extent by minerals or other material.

Based on the literature, the volume ratio of the initial acid to the whole emulsion (AMR) is a key factor for the characterization of emulsion stability and sludge formation. The experimental results for six Iranian crude oil samples showed that the most stable emulsion would form at equal values of AMR. In addition, more sludge was formed at higher acid volumes (Mohammadzadeh-Shirazi et al., 2019). Therefore, the equal volume ratio was selected for conducted experiments in this study.

2.4. Emulsion preparation and analysis

The required volumes of both acid and organic (crude oil or maltene) phases in separate bottles were firstly heated in an oven adjusted at 85 °C for about 10 min (the pre-heating step). For ferric ion tests, a certain mass of ferric chloride hexahydrate powder had to be added to the blank acid solution before pre-heating and homogenization by hand shaking the bottle to simulate the presence of the facility's corrosion product in a typical acidizing process. Acid and the organic phases were then mixed with a mechanical mixer at 1500 rpm for 30 s (emulsification step). These mixing conditions were chosen based on the previous works in the literature. It has been reported that the shear rate is in the range of 10–100 s^{−1} in the near wellbore region during a typical acid stimulation (Tie et al., 2019). Thus, mixing conditions ranging from 500 to 1500 rpm have been applied in the bottle tests to determine the acid-oil compatibility (Abbasi et al., 2023, 2024a, 2024b; Daghighi-Rouchi et al., 2025; Hedayati et al., 2023; Mohammadzadeh-Shirazi et al., 2019; Pourakaberian et al., 2021). Immediately, the whole emulsion was poured into a graduated 100-mL cylinder and placed in the oven. The phase separation was then recorded with time during 120 min after emulsification (data recording step). Finally, the stability of the formed emulsion was calculated based on the recorded data using the following equation (analytical step):

$$\text{Emulsion stability (\%)} = \left(1 - \frac{\text{Separated acid (mL)}}{\text{Initial acid (mL)}} \right) \times 100\% \quad (1)$$

2.5. Sludge separation and analysis

The materials in the cylinder (emulsion, separated acid, and flocs) were poured on a stainless-steel mesh of 140-μm pores. After separating the sludge from the liquid phase, it had to be washed with hot water and diesel before drying in an oven at 85 °C for 24 h. They help remove any remained emulsion and weak-adsorbed wax material from the sludge and more purification for accurate

measurement. Then, the net sludge mass was measured by an accurate digital scale with an accuracy of 0.001 g. Finally, Eq. (2) was used for calculating the sludge content for each test. The mass of the organic phase was then determined using its initial volume and the densities reported in Table 1. A summary of the complete experimental procedure is demonstrated in Fig. 1. To check the repeatability of the experiments, the reference tests for emulsion stability and sludge content were repeated three times for each sample (crude oil and maltene samples).

$$\text{Sludge content (\%)} = \frac{\text{Dried sludge mass (g)}}{\text{Initial crude oil or maltene mass (g)}} \times 100\% \quad (2)$$

3. Results and discussion

3.1. Emulsion stability

After contacting HCl with a certain crude oil (C1–C4), components having heteroatoms of oxygen, sulfur, and nitrogen would interact with acid ions causing various acid-base reactions to take place. As a result, a strong layer may be formed at the interface, which stabilizes the dispersed acid droplets. It is reported that this layer, which is mainly due to the protonation of some crude oil components, is not dissolved in a solvent, e.g. xylene (Garrouch et al., 2006; Houchin et al., 1990; Rietjens and Nieuwpoort, 2001). Therefore, the chemical structure of the stabilized interfacial layer is different from the original components of the crude oil, i.e. asphaltene, resin, and other natural surfactants. In some cases, this layer is composed of flocs that are large enough, so that they cannot pass through a micron-size mesh or even a filter paper which can be termed as acid-induced sludge (Kalhori et al., 2022).

Dynamic phase separation of the emulsions in Fig. 2 shows a higher (samples 2, 3, and 4 at the beginning) and faster separation rate (for all samples) in the case of acid-maltene emulsion than the acid-crude oil. It should be noted that in this study, full-phase separation in a short period of time was considered as the

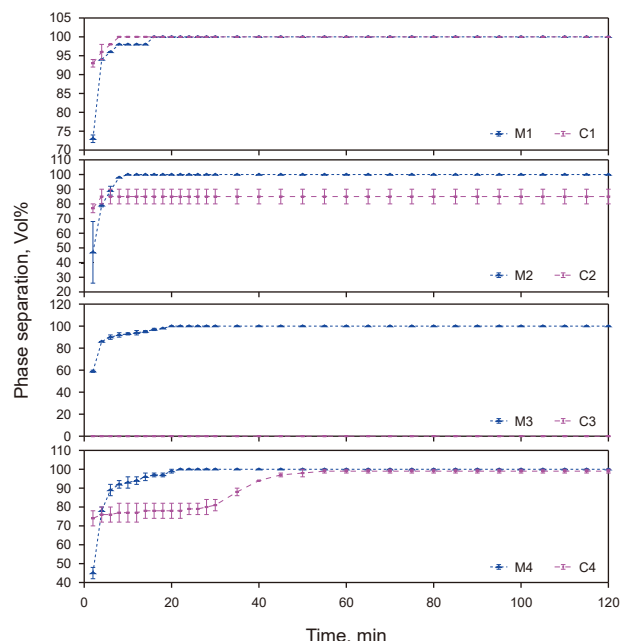


Fig. 2. Phase separation of emulsions versus time at the reference test conditions for crude oils (C1, C2, C3, and C4), and their respective maltene fractions (M1, M2, M3, and M4).

separation rate. This is due to the presence of a smaller number of surface-active components in the maltene compared with those in the crude oil. In fact, asphaltene molecules are absent in the extracted maltene. The HCl-oil emulsion stability is also affected not only by the amount of asphaltene as the most dominant natural surfactant in crude oil, but also by its properties and surface activity which originate from the molecular structure, and other components in the crude oil. For instance, based on the reported SARA data in Table 1, sample C1 had the highest asphaltene content while its CII was the lowest (1.06). This means that this asphaltene has a

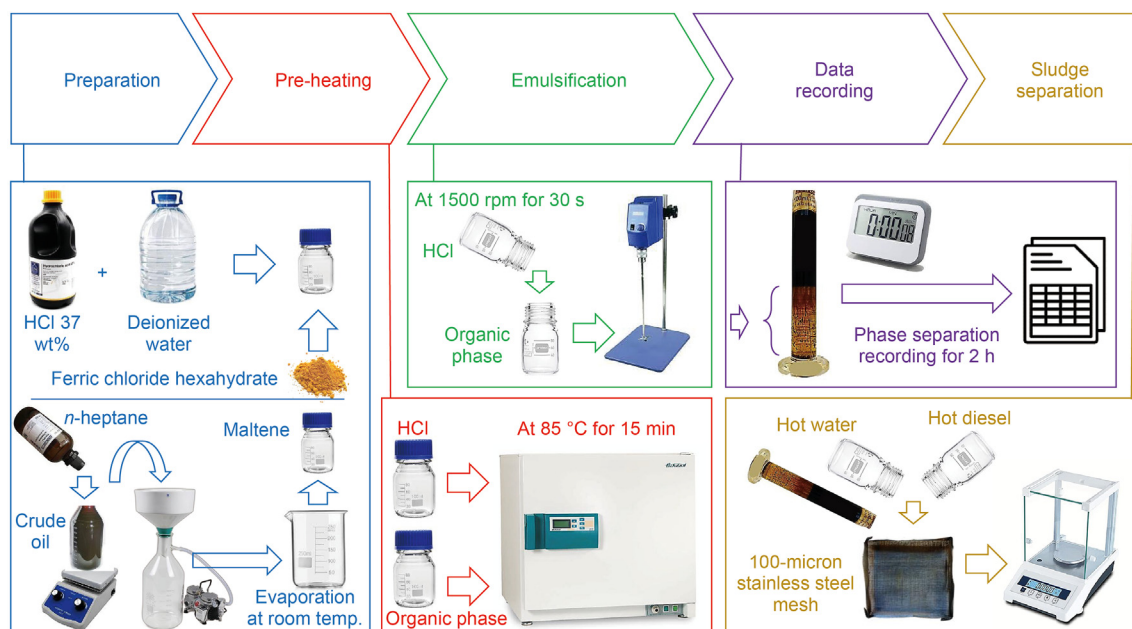


Fig. 1. Flowchart of acid-induced emulsion and sludge formation tests.

lower affinity to be adsorbed at the HCl-oil interface among the investigated samples.

As the experimental data points indicate and based on the field observations, the initial period of acid-oil contact is critical for interactions because of the acid strength (here HCl) and relatively fast reactions between acid ions and polar components in crude oil. In fact, forming the first rigid layer on the surface of the acid droplets happens in several minutes. In most cases except sample 4, no more phase separation happened after about 15 min of emulsification. As a result, the stability data at 15 min was used for evaluation of the emulsion stability.

To ensure the repeatability of the experimental data and to estimate uncertainties, the reference test for each sample was repeated. The mean values and error bars are presented in Fig. 3. Focusing on the data for the emulsions of maltene samples makes it evident that HCl-maltene emulsions do not tend to be stabilized. Except for the sample C1, all other HCl-crude oil emulsions showed higher stability with respect to the HCl-maltene emulsions. This observation confirms that emulsion formation is case-sensitive. This most likely depends on the asphaltene type and its characterization because the only difference between the crude oil and maltene samples is the presence of asphaltene. In fact, crude oil contains various fractions with a wide range of components. Therefore, it is hard to make a firm conclusion based on a limited number of experiments. It has though been reported in previous studies that the stabilizing role of asphaltene was more important than resin in acidic systems because of the negative surface charge and higher heteroatom contents (O, S, and N) (Abdollahi et al., 2014; O'Neil et al., 2015; Strassner, 1968). This, in turn, increases the affinity to interact with acid ions while resin stabilizes the oil emulsions in alkaline pH (Chaverot et al., 2008; McLean and Kilpatrick, 1997; Poteau et al., 2005). Sample C1 did not have a considerable affinity to react with acid under test conditions. Clearly, the only difference in chemical composition between the crude oil and its maltene samples is due to asphaltene. Therefore, such stability difference completely resulted from the activity of asphaltene molecules at the interface of acid and crude oil phases. On the other hand, surface-active properties of asphaltene make various emulsion stabilities for four crude oil samples that should be considered in future studies. The small difference in emulsion stabilities between the various maltene samples in Fig. 3 confirms that the chemical properties of maltene have only a meagre impact on the emulsion stability for the reference tests.

Emulsion stabilities at reference bottle test conditions (according to Table 2) for all samples are presented in Fig. 4 after 120 min. This figure helps to discern the emulsion stability over a longer

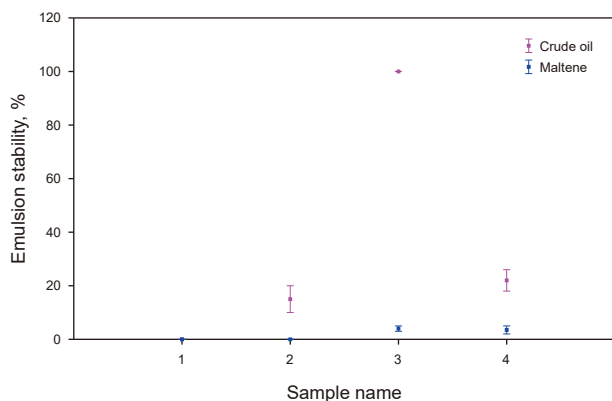


Fig. 3. Emulsion stability data and their repeatability for reference tests of crude oils and their maltene (experimental data at 15-min after emulsification).

period. In Fig. 4, the separated acid phase differs visually from the emulsion in color and light beam transmission. It has the color of yellow to light red while the acid-oil emulsion is dark color or black. It is obvious that all HCl-maltene emulsions were separated almost completely with negligible adhered sludge/precipitations on the cylinder wall. On the other hand, some amount of sludge or aggregates adhered to the glass surface of the cylinder because of more intense interactions of asphaltene in the crude oil with HCl. In addition, sample C3 formed a tight emulsion that did not break even after 120 min. However, the unstable asphaltene of this crude oil, known from the CII value based on the SARA analysis presented in Table 1, does not exist in the maltene sample M3. Consequently, as demonstrated in Fig. 4, a full-phase separation took place for this emulsion. In the case of sample C2, it is a bit blurred in Fig. 4 since part of the oil has adhered to the cylinder wall while 85% phase separation happened at the end of 120 min.

The results of HCl-crude oil or maltene emulsion stability at various experimental conditions are reported in Table 3. At a glance, the lower emulsion stability can be seen under most conditions for the maltene emulsions than the crude oil samples. It can be observed that maltene cannot form a stable emulsion at a higher pH of acid (lower than 7). In addition, its affinity to form a stable emulsion with a blank HCl solution can be neglected. In the case of ferric ion presence in the acid solution, the stability of maltene emulsions increased from 4% to 100% for different samples. It shows that ferric ions increase the contribution of the maltene components in stabilizing acid emulsions. It is believed that ferric ions have an affinity to oxygen-containing compounds of crude oil (Cotton et al., 1999), however, the effect of ferric ions has not been studied for maltene samples yet. The determination of colloidal instability index (CII) for maltene samples, like a crude oil without any asphaltene according to Eq. (3), results in 0.89, 1.35, 1.28, and 0.98 for samples M1 to M4, respectively. There may be a relation between the CII of maltene and its emulsion stability with acid in the presence of ferric ions in such a way that higher CII causes more activity of maltene. It can also be said that a higher saturate-to-aromatic ratio for maltene will result in higher precipitation affinity at the acid-organic phase interface and higher emulsion stability. This parameter shows the solvent nature of the maltene, neglecting resin effect (Mokhtari et al., 2022). Furthermore, it can be said that the stability of maltene emulsion is more sensitive to ferric ions than HCl. Similar results were observed for the crude oil samples. The undesired effect of ferric ions on the acid-induced emulsions and sludge have been reported in the previous studies for different crude oil samples. The increased emulsion stability stems from the molecular interactions, and various potential mechanisms were introduced so far to address this matter. For instance, one reason has been attributed to the catalyzing role of ferric ions in the polymerization of some hydrocarbons (Kovacic and Koch, 1963, 1965). Unstable ferric ion-complexes are able to catalyze oxidative polymerization of some species like pyrroles (Jacobs and Thorne, 1986; Speight, 2006). On the other hand, the electric charge of resin molecules may be neutralized by ferric ions, which results in destroying their stabilizing layer and lets asphaltene precipitate and accumulate at the acid-oil interface (Jacobs and Thorne, 1986; Speight, 2006). Moreover, several other works pointed to the phase transfer role of ferric ions in a system containing HCl and crude oil (Mirkhoshhal et al., 2021; O'Neil et al., 2015; Rietjens and Nieuwpoort, 1999; Rietjens and van Haasterecht, 2003). In this process, complexes like HFeCl_4 facilitate transferring of acids to the oil phase. Molecular simulation studies showed that hydrated ferric ions react with anions like chloride and produce water and HCl, which make the environment more acidic (Esmaeilbeig et al., 2022).

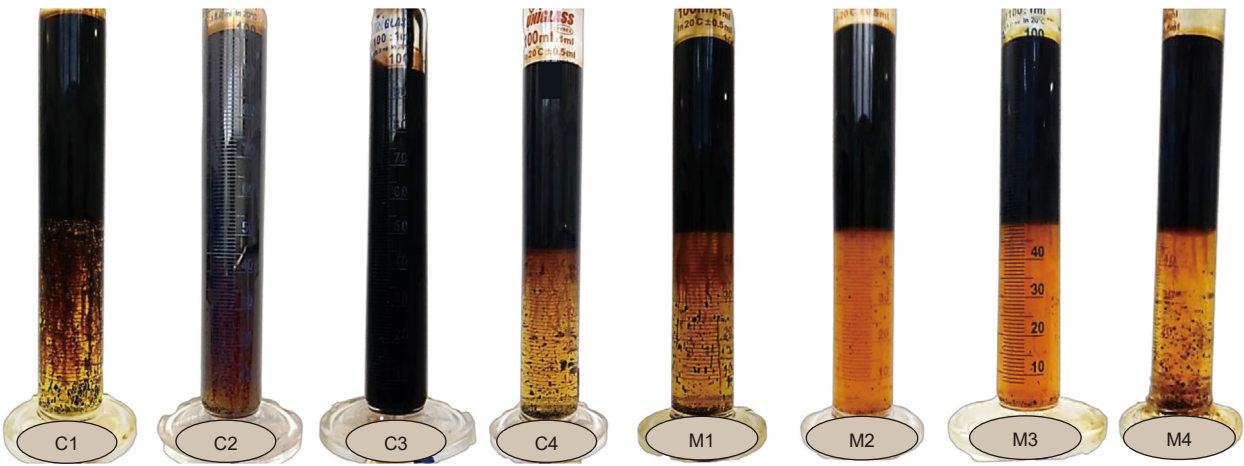


Fig. 4. Phase separation comparison of acid-crude oil and acid-maltene emulsions at the end of the experiment (120 min).

Table 3
Emulsion stability affecting ferric ion and pH at 15 min after emulsification.

Sample	Emulsion Stability, %		
	Reference test	[Fe ³⁺] = 3000 ppm	pH = 2
C1	0	10	0
M1	0	4	0
C2	15	100	2
M2	0	100	0
C3	100	100	59
M3	4	100	0
C4	22	100	0
M4	3.5	48	0

$$CII_{\text{maltene}} = \frac{\text{Saturate (wt\%)}}{\text{Aromatic (wt\%) + Resin (wt\%)}} \quad (3)$$

3.2. HCl-induced sludge formation

The mean values of sludge content and the uncertainty of experiments are shown in Fig. 5 for the reference tests. A negligible amount of acid-induced sludge was formed by all maltene samples

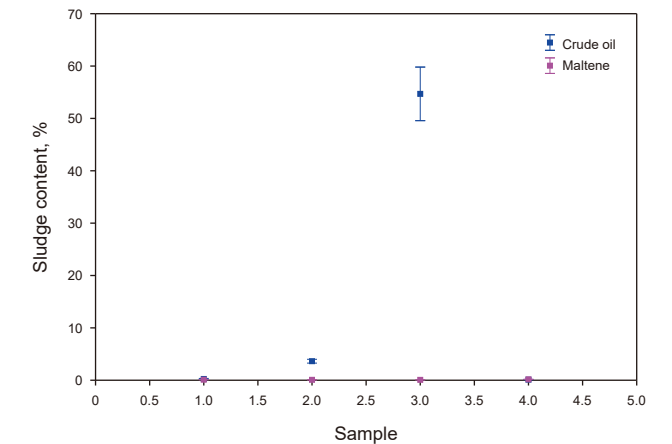


Fig. 5. Sludge content for reference compatibility tests of acid and crude oils or maltene.

for the reference test. In other words, maltene has no affinity to react with the blank acid. This outcome can be attributed to the polarity of maltene components. The only polar components in maltene are resin and naphthenic acids in small quantities, which have a much smaller polarity than asphaltene. On the contrary, asphaltene is the most polar component in crude oil, which is absent in the maltene (Arla et al., 2007; Lee, 1999). Therefore, in acidic conditions, such as contacting with a concentrated HCl solution, maltene has a small affinity to react with acid ions. On the other hand, sample C3 in Fig. 5, was affected by acid ions and some chemical interactions took place to form a considerable amount of sludge because of its unstable asphaltene, which does not exist in the maltene.

No formation of sludge for crude oil samples of C1 and C4, and their maltene (M1 and M4), in the absence of ferric ions, reflects that various components of these crudes did not react with the H₃O⁺ and acidizing can be a good treatment method for these crude oils. Although the components of maltene M3 have less affinity to form sludge in comparison to asphaltene, there is a high potential of sludge formation for C3, which means that its asphaltene is very sensitive to HCl. This observation indicates that acidizing may not be an appropriate treatment method for this sample.

Sludge formation under different experimental conditions is reported in Table 4. Almost in all cases and conditions, maltene produced less acid-induced sludge than their corresponding crude oil. Ferric ions increased the sludge formation for both crude oil and maltene samples. For the four maltene samples, higher sludge content of about 3.6, 46, 74, and 8.78 times formed in the presence of 3000 ppm of ferric ions with respect to the reference test without any ferric ions. These results indicate that ferric ions intensify the contribution of maltene components in sludge

Table 4
Sludge content of different samples for a given ferric ion and pH of acid solution.

Sample	Sludge content, %		
	Reference test	[Fe ³⁺] = 3000 ppm	pH = 2
C1	0.261	1.979	0.171
M1	0.094	0.459	0.154
C2	3.635	14.837	0.408
M2	0.079	3.733	0.150
C3	54.690	83.253	2.103
M3	0.073	5.518	0.333
C4	0.174	15.930	0.166
M4	0.227	1.698	0.124

formation. It is hypothesized that new acid-base interactions take place between acid ions and the polar groups of resin molecules by the catalytic role of ferric ions. The increased amount of sludge content at higher acidic pH (the situation during its neutralization of acid by reacting with the rocks or mineral scales in the reservoir), makes it clear that maltene would have more affinity to form sludge in contact with spent acid. It could be due to the non-polarity of maltene because generally, resin with a small mass fraction is the only high polar component in maltene. Therefore, the more concentrated acid cannot cause a high sludge formation in contact with maltene components. It was reported that asphaltene has a high surface activity at acidic pH, while the surface activity of resin, which is present in the maltene, is much lower (Strassner, 1968).

Pourakaberian et al. (2021) showed that there is not a meaningful proportionate relation between the amount of heavy components in crude oil such as asphaltene, and the amount of formed sludge. This can be substantiated from the results that are presented in Table 4 for sample C1 with the highest asphaltene content of 8.1 wt% among the four crude oil samples. The extent of formed sludge can visually be seen in Figs. 6–8 under different test conditions. Such visual comparison will help to better understand the causes of sludge formation. As Fig. 6 demonstrates, the amount of acid-induced sludge is negligible for the maltene of all samples in comparison with the crude oils for reference tests. Based on a classification for the acid-induced sludge suggested by Mohammadzadeh Shirazi et al. (2019), it can be seen that samples C2 and C3 had a voluminous mass of sludge, referred to as the “slurry and plastic” type, while their maltene did not form a considerable volume of sludge. On the contrary, samples C1 and C4 formed a small amount of sludge, which is classified as the “lumped” type.

Similarly, Fig. 7 shows the formed sludge in the presence of ferric ions in the HCl solution for the investigated samples. According to these photos, ferric ions promoted the mass and volume

of formed sludge for all samples. It means that either for crude oil or maltene samples, more chemical interactions take place between acid ions and the organic material in the presence of ferric ions. A comparison of photos in Fig. 7 with Fig. 6 confirms that for samples C1 and C4 with negligible sludge in the absence of ferric ions, considerable amounts of sludge were formed due to more interactions with ferric ions. Therefore, ferric ions are able to involve non-polar components of the crude oil in the formation of acid-induced sludge. Moreover, samples C1 and C4 in the presence of ferric ions in the acid solution formed a “slurry and plastic-type” sludge. It means that ferric ions can improve the formed sludge even in cases with no affinity to react with the blank HCl solution.

An interesting point to discern is the effect of higher acidic pH (spent acid) on sludge formation. This situation happened in the reservoir because of the neutralization of injected acid due to acid reaction with different materials such as rock minerals and clogging precipitates. It can be seen in Fig. 8 that a higher sludge formation took place for the crude oil samples. Increasing the acidic pH (more acid neutralization in the reservoir) had only a marginal impact on the formed sludge for different maltene samples, whereas considerable differences were obvious between the crude oil samples. It reaffirms that the asphaltene role, which does not exist in maltene, is affected by acidic conditions, such as pH in this study. Having said so, some other conditions such as ferric ions have a considerable impact on the acid-induced sludge formation, as it was mentioned earlier in Fig. 7.

Figs. 6–8 confirm categorically that asphaltene is the most dominant factor in acid-induced sludge formation. The other much less polar components of the crude oil such as resin and naphthenic acids cannot make a severe problem in the absence of asphaltene, except in the presence of ferric ions.

It is better to describe the contribution of maltene to sludge formation from the perspective of acid-crude oil contact and mixing. For doing so, the following equation is proposed to make a

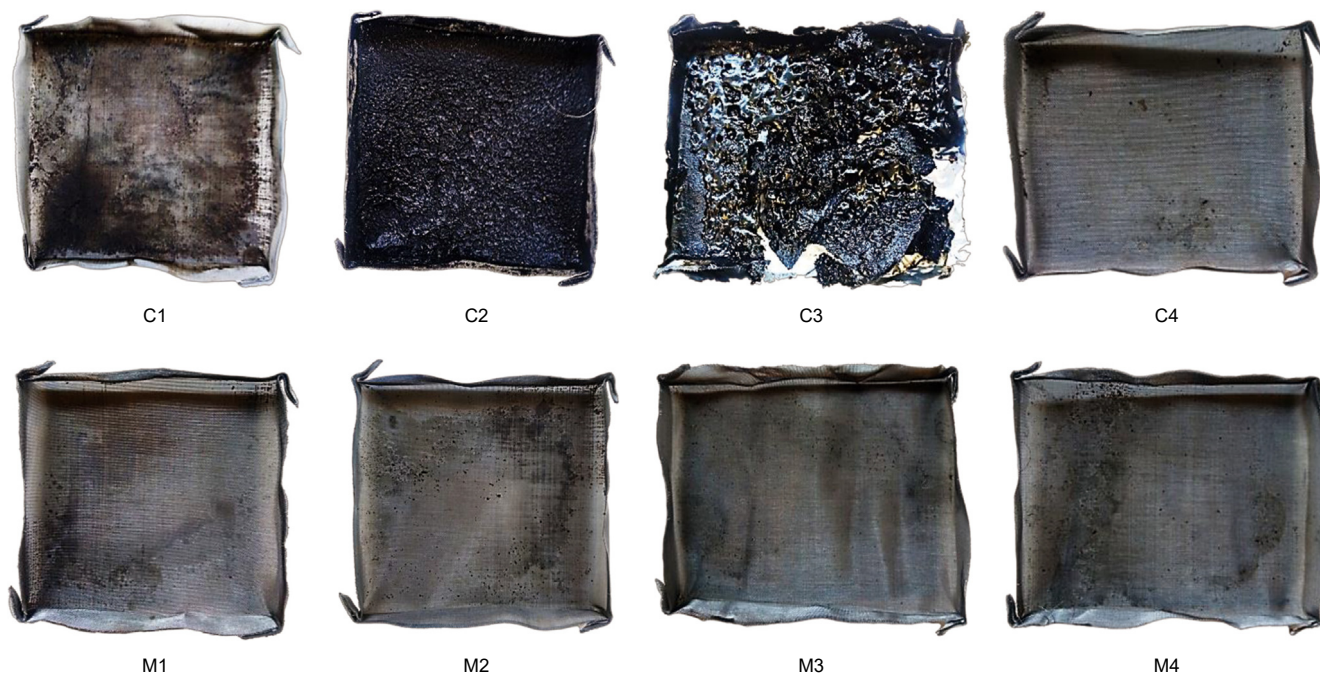


Fig. 6. Acid-induced sludge formed in reference tests for the crude oils and their maltene.

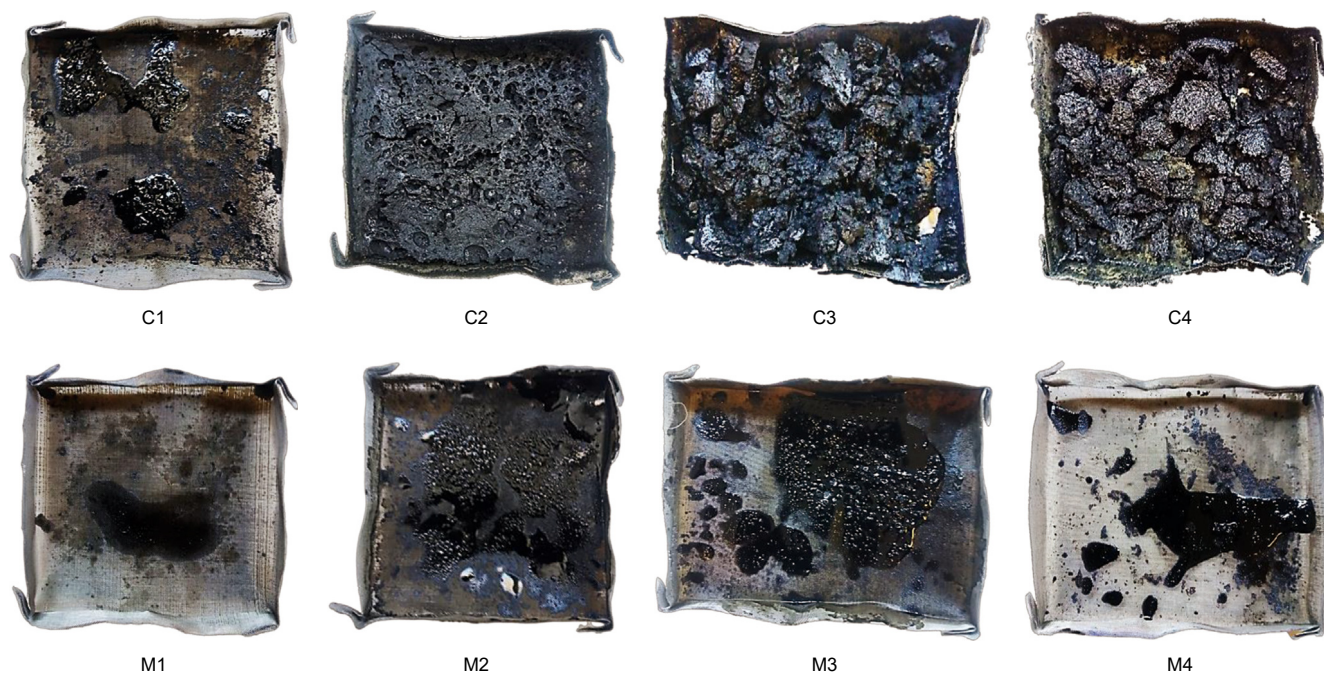


Fig. 7. Impact of ferric ion on acid-induced sludge formation for the crude oils and their maltene.

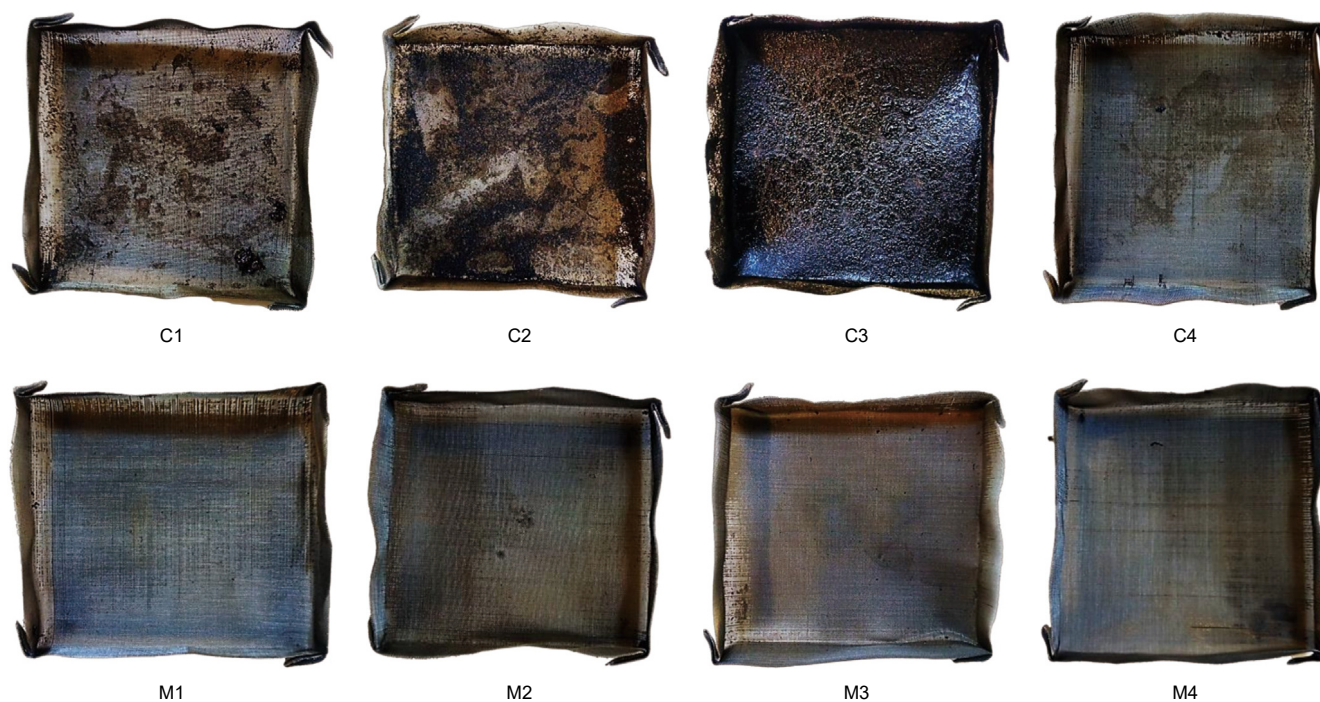


Fig. 8. Acid-induced sludge formation for the crude oils and their maltene using an HCl solution with a pH of 2.

comparison between formed sludge from each crude oil and its maltene sample. The results are presented in Fig. 9 for all samples.

Fig. 9 shows that for the reference tests, maltene has a small contribution to acid-induced sludge formation during mixing with 15 wt% HCl solution, except for sample C4, which could be caused

$$\text{Maltene contribution to sludge formation (\%)} = \frac{m_{\text{maltene sludge}} (\text{g})}{m_{\text{crude oil sludge}} (\text{g})} \times 100\% \quad (4)$$

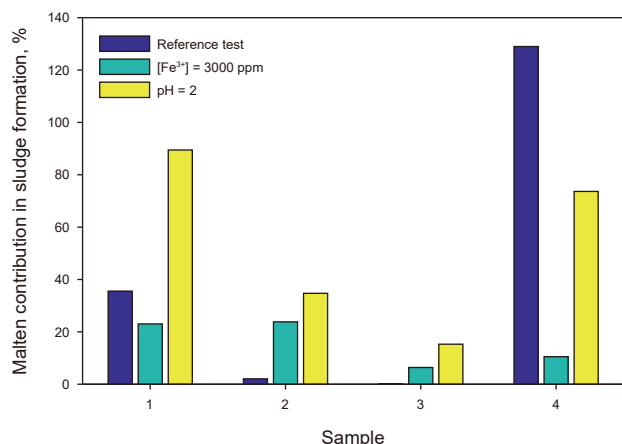


Fig. 9. Maltene contribution to sludge formation at various test conditions based on Table 4.

by the high resin-to-asphaltene ratio of 4.6 in the crude oil. Resin molecules act as peptizing agents for asphaltene and would help it to be dispersed better in crude oil. As a result, it is expected to observe less surface activity from asphaltene. This explanation may be the reason for the higher sludge content of M4 than C4 in Table 4 and the 130% contribution of maltene in sludge formation. There may be some interactions between asphaltene with the other components in the crude oil, which there are not in maltene. Therefore, more components would react with the acid phase in the absence of asphaltene, and more sludge would form for the maltene. A better insight and explanation for this exception requires further thorough chemical characteristics of the SARA components in the crude oil and the formed sludge, which is presently under study.

It is also evident from Fig. 9 that when the pH of the acid solution becomes 2, then a contribution of 20% to almost 80% of maltene components to sludge formation would be expected. As stated before, maltene, which contains a small amount of resin along with a higher amount of non-polar saturate and aromatic components, may have more affinity to form sludge in less acidic conditions. Previously, it has been reported that de-asphalted crude oils can form sludge during acidizing (Rietjens, 1997).

According to Fig. 9, ferric ions intensify the contribution of maltene in sludge formation. Several chemical reactions have been suggested in the literature between ferric ions and some components of the crude oil such as pyrrole, pyridine, porphyrin, and phenolic hydroxyl groups, which have mostly heteroatoms in their structures (Jacobs and Thorne, 1986; Rietjens, 1997). In the case of maltene, it can be said that negligible amounts of heteroatoms exist. Thus, these reactions may not take place. However, some mechanisms proposed take place at the interface of acid and crude oil including ferric ions (Ganeeva et al., 2020). The first mechanism is the adsorption of ferric ion complexes composing ferric cations and polar groups of asphaltene molecules. The second mechanism is the phase transfer behavior of ferric ions for acid ions to the interface and to the organic bulk. For non-polar components of maltene, the first mechanism may not be applicable since ferric ions interact with polar molecules, which are absent in the maltene. The second mechanism, which emphasizes on catalytic role of ferric ions (Rietjens and van Haasterecht, 2003), seems to be more realistic in the case of maltene. It can be inferred that ferric ions act as catalysts because they increase considerably the emulsion stability and sludge content according to Tables 3 and 4, while the intensified contribution of maltene to the sludge content is only up

to 20% for all samples, as shown in Fig. 9. In other words, they may not contribute to the sludge formation and just act as an intermediate component for the acid-organic components interactions. To prove this conclusion, some chemical analysis should be performed to investigate the amount and the chemical bonds between ferric ions and the organic components of the crude oil. The concept of interface structure is profoundly imperative in the fluid flow behavior, especially in acid stimulation that includes liquid-liquid and liquid-solid interfaces (Hong et al., 2023). After acid injection in the reservoir and its contact with crude oil, they interact according to the operational conditions and existing chemical species. Natural surfactants such as asphaltene, resin, and naphthenic acids start moving towards the acid droplets, i.e. the acid-oil interface, through several mechanisms and interactions that discussed before in the literature and also the present study. Ferric ions as phase transfer catalysts improve acid ions mass transfer to the interface and enhance the acid-base interactions (Mirkhoshhal et al., 2021; Mohammadzadeh-Shirazi et al., 2019; O'Neil et al., 2015; Rietjens and Nieuwpoort, 1999; Rietjens and van Haasterecht, 2003). Therefore, natural surfactants accumulate at the interface and form a strong and viscous stabilizing layer, known as sludge, which increases the acid-oil emulsion stability. This interfacial film causes higher viscosity and stickiness, adhering to the formation rock and change its wettability, postpone the acid-oil phase separation, and affect negatively the flow ability of the fluids in the porous medium. Moreover, some chemical additives, which are widely used in a typical acid stimulation process, may be inconsistent with each other and precipitate by forming flocs. Therefore, it is crucial to focus on the interactions and mechanisms that influence on the interface and natural surfactants behavior in the acidic medium, especially in the presence of ferric ions.

Finally, the comparison of emulsion stability and sludge content between different crude oils and their maltene samples showed that asphaltene, as the most polar and surface-active component in crude oil, plays a key role in emulsion and sludge formation. In addition, there are some conditions, such as acid neutralization to a higher pH and ferric ion presence in the acid solution, that improve the contribution of de-asphalted crude oil to emulsion stabilization and sludge formation. The intensity of acid-crude oil interactions would be different on a case-to-case basis and all of the crude oil components play different roles in various conditions. The study of the chemical composition of the dried sludge from the acid-crude oil mixing and the extracted asphaltene from the crude oil besides their structure can provide a better insight into interactions between acid and crude oil.

4. Conclusions

Experimental data points, in the open literature, on acid-induced emulsion stability and sludge formation for maltene are scarce. In addition, the contribution of maltene constituents in acid-oil interactions, which would potentially result in emulsion and sludge formation, is the key novelty of the present study. Accordingly, in this study, the compatibility of four crude oil samples and their maltene with HCl solution of 15 wt% at different pH conditions and ferric ion presence has been investigated. Based on the experimental results, crude oils formed considerably higher stable emulsions with respect to their de-asphalted samples, about 6–25 percent higher in the presence of blank HCl. Furthermore, a completely stable emulsion formed only in the case of crude oil while no emulsion remained after 15 min for the maltene samples. In other words, de-asphalted crude oil showed only a meagre affinity to react with the blank HCl or ferric ion-free spent acid to stabilize the emulsion. In addition, ferric ions promoted HCl-crude oil/maltene emulsion stability from near zero to the level of no

phase separation, most likely through a catalytic mechanism. However, more studies on chemical analysis would be required before making a firm conclusion. In all tests, sludge formed along with stable emulsion, a result that contradicted some of the previous studies, which reported only one of them takes place for a certain crude oil. For maltene samples, ferric ions increased the sludge formation between 4 and 75 times in comparison with the blank HCl. Nonetheless, the contribution of de-asphalted crude oil components to sludge formation was less than 20% of crude oil's total sludge. It showed that among the various components of crude oil, asphaltene plays a key role in the formation of stable emulsion. Chemical analysis of the formed sludge can provide better insight into the actual interactions between ferric ions and crude oil components. However, maltene contribution to sludge formation increased between 15% and 90% for the case of spent acid with a pH value of 2. The non-polarity of most components of the de-asphalted part and the catalytic role of ferric ions may account for higher sludge formation at these conditions.

CRedit authorship contribution statement

Ahmad Abbasi: Writing – original draft, Visualization, Software, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **M. Reza Malayeri:** Writing – review & editing, Validation, Supervision, Conceptualization, Project administration, Resources. **Maysam Mohammadzadeh Shirazi:** Writing – review & editing, Validation, Methodology, Conceptualization.

Data availability statement

All data generated or analyzed during this study are included in this published article.

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