

Article

Quantifying the Effect of De-Emulsifiers on Acid Treatment in Carbonate Formations

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Abstract: Matrix acidizing is a highly successful, effective, and relatively inexpensive approach to enhancing well productivity in carbonate formations. Accordingly, there has been little motivation to address the ways to optimize the acid stimulation process better. Acid-in-oil emulsions that form during this process cause one of the most challenging problems that negatively impact the performance and deliverability, especially when these emulsions are highly stable over extended periods. Such stable emulsions can plug the flow path of oil causing high resistance to flow and potentially reducing well productivity. De-emulsifiers are some of the most widely used acid additives targeting the reduction of emulsion stability. However, there is doubt in the research community on whether there is enough shear mixing that can cause the formation of emulsions inside the rock matrix. Besides, the effectiveness of de-emulsifiers in eliminating such emulsions in the pore space has not been investigated. In the current oil price market, there is a need to be more vigilant regarding the cost of well stimulation and the added value from the various additives. While laboratory work on matrix acidizing in carbonate formations is abundant, the work on oil-saturated samples is rare, and therefore, the effect of emulsions on the acidizing process has not been widely documented. In this work, we present a stacked study of bottle tests and core flooding tests designed to investigate the de-emulsifiers' role in the rock matrix. The results reveal that (1) emulsion-risk in the pore space is real, and (2) the addition of de-emulsifiers to the acid allows for efficient backflow of oil, revealing an improvement in the performance of the acidizing treatment.

Keywords: de-emulsifiers; acid-in-oil emulsions; carbonate acidizing; acidizing additives



Citation: Elsafih, M.; Fahes, M.; Teodoriu, C. Quantifying the Effect of De-Emulsifiers on Acid Treatment in Carbonate Formations. *Energies* **2021**, *14*, 1148. <https://doi.org/10.3390/en14041148>

Academic Editor: Attilio Converti

Received: 28 January 2021
Accepted: 19 February 2021
Published: 21 February 2021

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1. Introduction

The concern about the negative effect of crude oil emulsions in the petroleum production system has been documented for decades [1–5] and is still being addressed in recent years [6]. Emulsions can cause many obstacles throughout the production system, starting from the formation to the refining unit [3,7]. When the emulsions form and settle in the formation, they can block the pores and resist the oil flow toward the wellbore resulting in less productivity [8], while its accumulation in the production pipes or flowlines can cause an unwanted high-pressure drop [9]. Besides, the high viscosity of these emulsions can cause the pumping system's failure or, at the least, increase the cost of maintaining. If emulsions are allowed to reach the final stage of the production system (refining and transportation), the process of extracting the oil is difficult and costly [3,7,10]. Although major emulsions form when water mixes with oil, data from field cases of acidizing reveals the formulation of emulsion post acidizing [1,11,12]. In 1965, a very thick emulsion was produced from acidized wells in the Virginia Hill D-3 reef oil pool in Canada [1]. Studying the history of acidizing in Canada from 1970 to 2009, Knopp [12] concluded that spent-acid emulsions and asphaltene sludge cause post-acidizing damage of formations such as Swan Hills.

Crude oil emulsions are generally classified as either macro or microemulsions, where microemulsions can be identified as water in oil, oil in water, and multiple emulsions, whereas macro emulsions are classified as either single or double emulsions [13,14]. Under

fixed temperature conditions, such emulsions' stability depends mainly on two factors: the water-oil interfacial tension and the time since mixing occurred [15–17]. Previous studies have shown that crude-water emulsions are dynamically stable, where their stability and viscosity decrease with time [15,18–21]. However, our previous work has shown quantitatively that crude-acid emulsions' viscosity can increase with time [22]. Previous research has shown the essential need for acid treatment additives such as corrosion inhibitors, solvents, dispersants, anti-sludging agents, and de-emulsifiers [1,23–26]. De-emulsifiers are typically used to mitigate the effect of crude oil emulsions on well deliverability. De-emulsifiers in the oil and gas industry are available in many categories, such as organic vs. inorganic matter, micro-molecules vs. macro-molecules, and ionic vs. nonionic types. A good de-emulsifier must have the following criteria [27,28]: first, an ability to migrate quickly through the oil phase and successfully compete against considerable odds for its place at the water–oil interface. The de-emulsifier's intense attraction to water will force different water droplets in the same condition to pound together as larger droplets of water. This mechanism is called flocculation. Finally, de-emulsifiers should stabilize the films surrounding the large water droplets, allowing them to unite, called coalescence.

Many studies show the advantages of using emulsified acids to reduce acid reaction rate and achieve deeper penetration [29,30] or as diverting material to prevent acid from flowing to high permeability zones [31], resulting in a more efficient wormhole propagation. However, the impact of emulsions on the flowback of oil into the wellbore has not been documented. Natural emulsifiers in some crude oils make them more prone to emulsifying with water or formation brine [32,33]. However, even oils that do not form stable emulsions with water can still form very stable emulsions with acid [22]. Matrix acidizing technique, where acid is injected into the formation and mixes with crude oil, is proven to be a successful method of improving the productivity [34]. However, this mixing leads to very stable emulsions that can plug the pores and adversely affect the oil flow efficiency into the wellbore post acidizing [22,35,36]. The emulsion problem during acidizing experiments is not commonly captured in laboratory studies because a vast majority of these experiments are conducted with water-saturated cores [37,38]. However, in reality, oil is still present in pores when acid is injected, even if a water pre-flush is applied. Shukla et al. [39] highlighted the effect of oil or gas presence in the saturation on acidizing optimization. They showed that the presence of an immiscible phase, whether oil or gas, affects wormhole propagation, resulting in less branching. Besides, oil saturation has a significant impact on lowering the acid optimum injection rate and minimizing the volume of acid needed. The possible role of emulsions in this process has not been addressed in the literature.

In this work, experiments were conducted to quantify the de-emulsifiers' effect on oil flow performance after acidizing. A crude-oil from a field in Texas was obtained for this study, and Indiana Limestone was used in the flooding tests. Nine different de-emulsifiers were investigated to identify the most effective one in eliminating the emulsion, and bottle tests were conducted to study the stability and viscosity of three fluid systems. A core flooding experiment was designed that replicates the process of well stimulation as well as flowback and oil production. The analysis of pressure and rate data was performed in the case of emulsion-prone fluid systems and emulsion-free fluid systems. The details of the materials used, experimental procedures, and results and discussions are shared next.

2. Materials and Methods

2.1. Materials

2.1.1. Indiana Limestone Core

A 0.156 m in length (6 inch) and 0.038 m in diameter (1.5 inch) sample of an Indiana Limestone was cored using water-based drilling and then dried. Its porosity was measured using a helium porosimeter as 16% and absolute permeability using nitrogen gas as $5.428 \times 10^{-13} \text{ m}^2$ (55 mD).

2.1.2. Crude Oil

A crude oil sample was purchased from Texas Raw Crude to be used in this study [9]. The dynamic viscosity was measured using a cannon capillary viscometer to be 0.0256 Pa.s (25.6 cp). The density was measured using a pycnometer to be 880 kg/m³.

2.1.3. Hydrochloric Spent-Acid

Live-acid was used in order to prepare a spent-acid solution for use in this work. 37 wt.% HCl solution obtained from Sigma Aldrich was first diluted to a 15 wt.% acid, which is typical for carbonate acidizing. Chunks of Indiana Limestone (>99% calcium carbonate) were used to fully spend the acid, as shown in Figure 1a, so that it does not have any more dissolving power. The spent-acid was then filtered, as shown in Figure 1b, to remove impurities and obtain the final spent-acid used in the bottle and flow tests. The spent-acid pH was measured to be 5, which is close to the 4.5 pH value typically measured for spent-acid during flowback in the field [40].

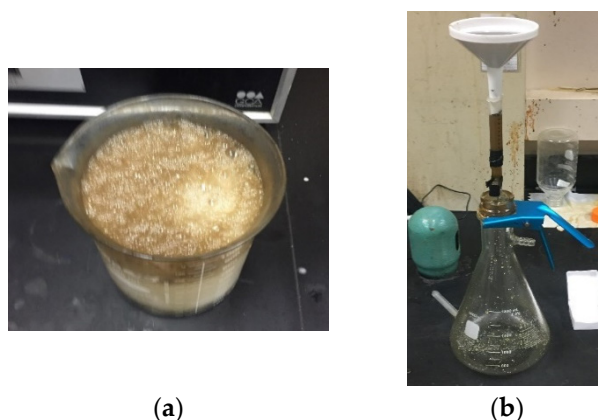


Figure 1. Spent-acid preparation. (a) Live acid reacting with Indiana Limestone chunks; (b) filtering the resulted spent-acid.

2.1.4. De-Emulsifiers

A set of nine de-emulsifiers was tested using a simple bottle test to examine the effectiveness in limiting the formation of an emulsion between acid and crude oil. These de-emulsifiers were obtained from a vendor without identifying the content. Live acid was used in these tests given that the emulsion between crude oil and live-acid is the more viscous and stable emulsion.

2.1.5. Surfactant

In some of the experiments, there was a need to add a surfactant into the oil which acts as an emulsifier, in lieu of naturally occurring surfactants. The surfactant used for this purpose was span-85.

2.2. Experimental Setup and Procedures

In this section, we describe the experimental setup and procedures used in this work. The bottle tests used to evaluate the de-emulsifiers' effectiveness are first described, followed by the procedure used to quantify the effect of a de-emulsifier on the stability and viscosity of emulsions. After that, the core preparation method and the flooding experiments are presented.

2.2.1. Bottle Tests for Screening De-Emulsifiers

Bottle tests were used to screen the de-emulsifiers and identify the effective ones in inhibiting emulsification between live acid and crude oil. A total of 5 cc of fluids was placed in a vial with a 3:7 volumetric ratio of live acid to crude oil. 1 wt.% of de-emulsifier

was added to the acid before mixing. The small vial was then vigorously hand-shaken for five minutes and then placed on a counter. The separation of an oil or an acid phase was then observed. While the emulsifier concentration can impact its effectiveness, the goal of this step was not to identify the best or optimum concentration but to quickly screen for an effective de-emulsifier. This goal was achieved, and thus there was no need to test the variations in concentration.

2.2.2. Bottle Tests for Emulsion Viscosity and Stability

Bottle tests were also used to study the emulsification behavior of three fluid systems used in this study. These tests included creating a total of 150 cc of mixture for each fluid system using an emulsion study protocol developed by our team that proved to result in reproducible emulsions to allow for consistent experiments [32]. A homogenizer was used to mix the emulsion for 30 min at 5000 rpm. The 150 cc of emulsion was then divided into five different vials. The first vial was used to capture the viscosity of the emulsion after mixing. The other four vials were observed at time intervals of 5 h, 24 h, 3 days, and 5 days. At each time interval, the separation was observed, and then a sample was recovered from the top of the emulsion to collect viscosity information.

The three studied fluid systems were: (1) Spent-acid + Oil (a system not prone to emulsions), (2) Spent-acid + Oil, and 1 wt.% Surfactant (a system prone to emulsions), and (3) Spent-acid and 1 wt.% de-emulsifier + Oil and 1 wt.% surfactant (where the effectiveness of the de-emulsifier in eliminating emulsions is documented).

2.2.3. Core Preparation Procedure

The goal of the core flooding work is to quantify the emulsion effect on the flowback of oil after acidizing. This requires the propagation of a wormhole only part of the way through the rock and then injecting oil from the other side of the core. In previous work [22], an attempt to inject live acid into the core to generate a partial wormhole was challenging as no visible wormhole entry was observed. Accordingly, we designed a simple experiment to allow the study of the flowback process of spent-acid and oil without having to go through live-acid injection. A small hole was drilled into the core to represent a wormhole. In order to use the smallest of the drill bits, we cut two 1-inch length pieces from the inlet of the core, as shown in Figure 2a, and used a 1/16-inch drill bit to drill a hole in the two inlet pieces. The image shown in Figure 2b shows the drilled hole's width compared to a wormhole casted in a different core after live-acid injection. To limit the number of factors that can influence the experiment's reproducibility and simplify the analysis process, this work was performed with no initial water saturation and at room temperature. With this being the first study of its kind, the impact of variable initiation saturation and temperature can be deferred to future studies.

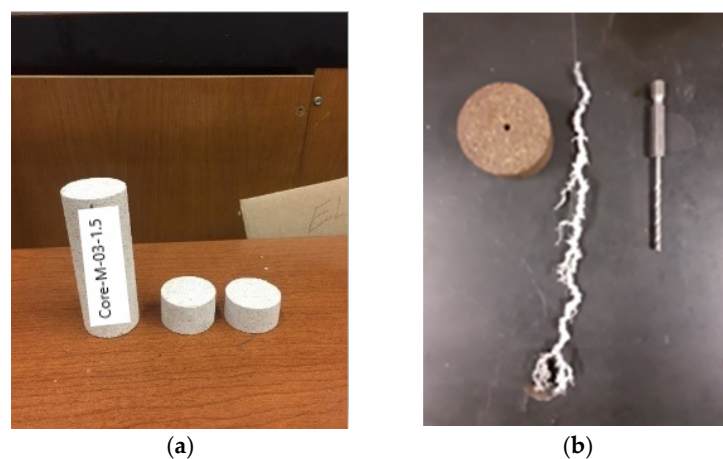


Figure 2. Core preparation. (a) Core is cut and drilled; (b) the 1/16-in drill bit used to simulate a wormhole.

2.2.4. Core Flooding Tests

After the core was prepared, it was saturated with crude oil using a vacuum cell. The core-flooding procedure involved packing the three pieces of the core in series with the two drilled pieces placed at the inlet of the core. Three phases of injection were then conducted using the setup shown in Figure 3. The setup consists of an ISCO injection pump, an acid accumulator, an oil accumulator, a core holder, pressure gauges, and a confinement pressure pump. The injection pump was used to flood oil or acid from accumulators into the core while the confinement pump is applying a 2000 psi pressure around the core. Pressure gauges were monitored to collect the pressure responses data for each injection.

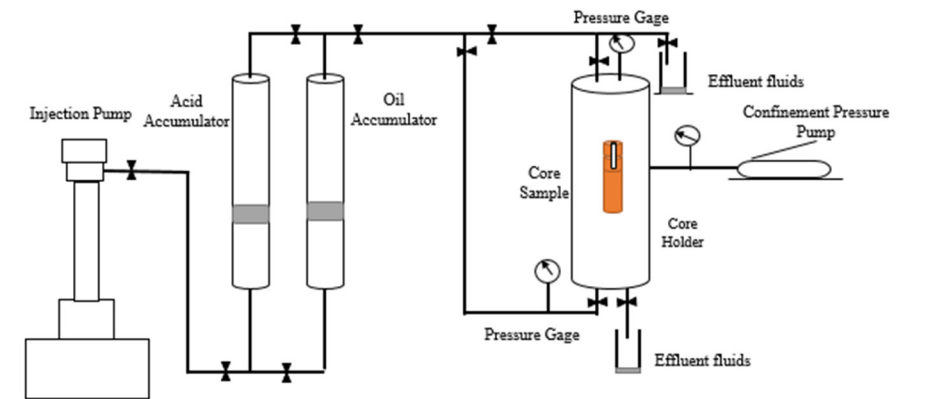


Figure 3. Core flooding setup schematic.

Oil was injected from the core inlet at a constant rate of 1 cc/min to establish a pressure profile and oil mobility after the initial vacuum-saturation process. This was followed by spent-acid injection at the core's inlet at the same rate of 1 cc/min. The last phase was oil injection from the back of the core, also at 1 cc/min. Three such flooding tests were conducted along the same lines as the bottle test experiments: (1) Spent-acid + Oil, (2) Spent-acid + Oil and Surfactant, and (3) Spent-acid and de-emulsifier + Oil and surfactant. At the end of each test, the core was exposed to a cleaning process using cycles of toluene and methanol to extract the fluids in preparation for re-saturating with crude oil to conduct the next experiment. The data collected are the profiles of pressure build-up during injection, which documents the resistance to the injected phase flow. The pressure gauge used in this flooding setup had a maximum pressure rating of 2×10^6 Pa (300 psig); accordingly, the injection was halted when that pressure was reached.

2.3. Assumptions and Limitations

There were some assumptions and limitations that the authors want to layout for consideration. The first is that the work assesses the transitional pressure build-up and not the steady-state flow in the displacement process. While this is a critical stage of the acidizing and the acid cleanup process, this limits the conclusion to that unsteady-state displacement phase. The work was performed at room temperature to simplify the experimental workflow and limit the variables investigated in this study. When this workflow is being used to quantify a de-emulsifier's impact on a particular rock-fluid system for field application, it is vital to perform these experiments at reservoir temperature and injection pressure conditions [41]. One assumption that was made was that the drilled hole represents a wormhole. This is a valid assumption given that the hole's diameter is similar to that of an actual wormhole generated during optimum acid injection conditions. One expects the wormhole generated in oil-saturated cores not to have branches, and that supports the validity of the assumption.

3. Results and Discussion

3.1. Bottle Tests for Screening De-Emulsifiers

These tests' goal was to identify an effective de-emulsifier to use in the rest of this study. The formation of emulsions was observed over 24 h. Various amounts of thick emulsion were observed for each of the various de-emulsifiers, as shown for select samples in Figure 4a–c, except for de-emulsifier #7, in Figure 4d. Accordingly, de-emulsifier #7 was used in the remainder of the study and is referred to as merely “de-emulsifier” henceforth in the paper.

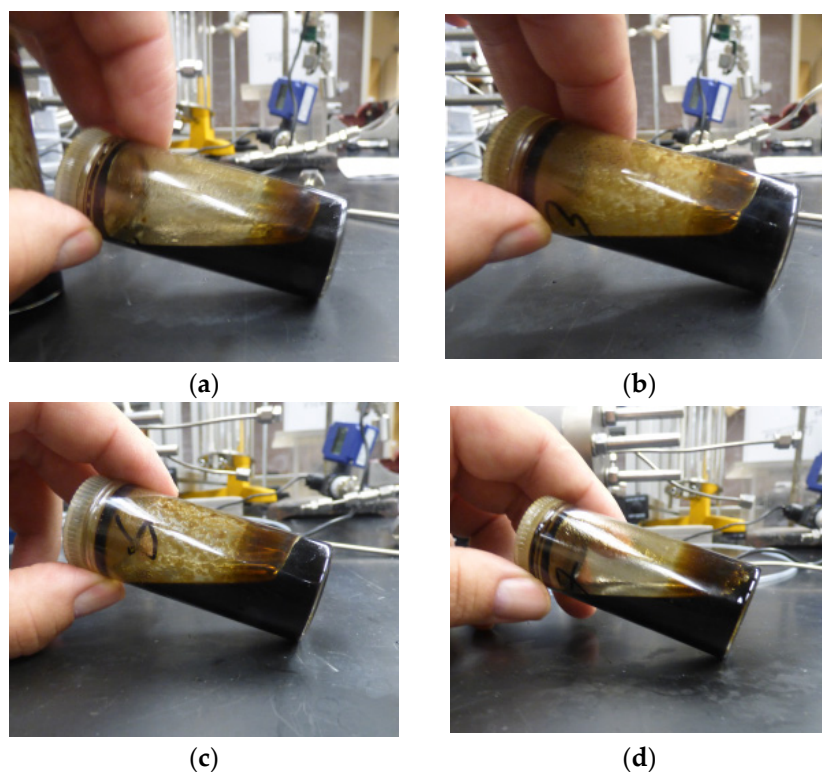


Figure 4. Images taken after 24 h of mixing, showing the presence of a thick emulsion (sludge) at the bottom of the vial for (a) de-emulsifier 1, (b) de-emulsifier 3, and (c) de-emulsifier 6, and the absence of a thick emulsion in (d) de-emulsifier 7.

3.2. Bottle Tests for Emulsion Stability and Viscosity

This set of bottle tests was designed to answer two questions: (1) while this oil emulsifies with live-acid, does it actually emulsify with spent-acid to allow us to use this experimental design for studying the backflow behavior after acidizing? Furthermore, (2) Does the de-emulsifier work in breaking these emulsions between the oil and spent-acid?

The first set of experiments between the oil and spent-acid showed that although an emulsion does form, it was not a stable emulsion. Acid separation can be seen at the bottom of the vial in Figure 5a. This was expected since this oil does not emulsify with water. A surfactant that had been proven in our previous work to result in stable water-in-oil emulsions [33] was added to the oil sample. The result of mixing spent-acid with the “oil and surfactant” is shared in Figure 5b. It shows that there was no separation observed even after 5 days from the time of mixing. The last image, shown in Figure 5c, shows the separation resulting from using the de-emulsifier in the spent-acid and mixing it with the “oil and surfactant.” These results established for us three scenarios: (1) A case of spent-acid and oil that is not prone to emulsions; (2) a case of spent-acid and oil that is prone to emulsions (presence of surfactant and absence of de-emulsifier); and (3) a case of spent-acid and oil that is typically prone to emulsions, but where a de-emulsifier is added to control for these emulsions.

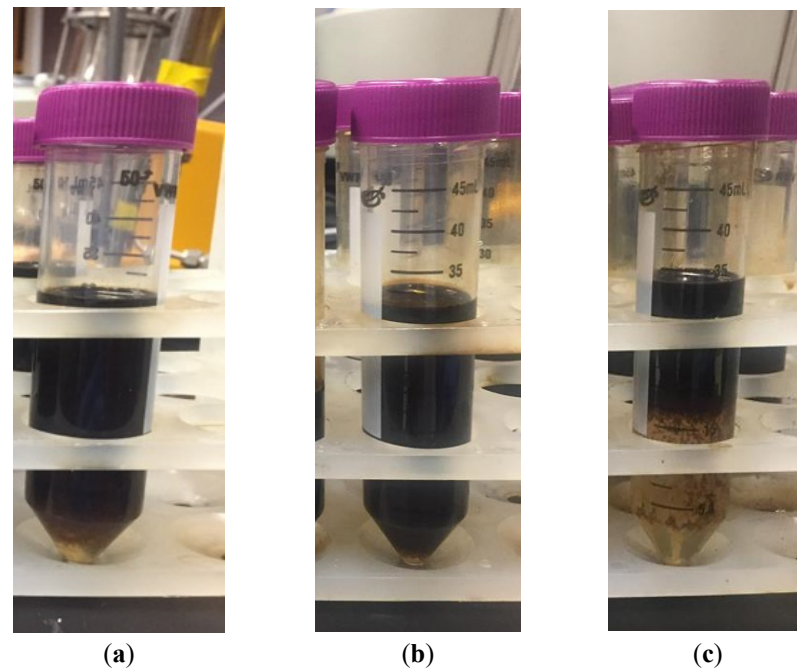


Figure 5. Separation of spent-acid oil emulsion after 5 days whereas (a) spent-acid is mixed with crude oil; (b) spent-acid is mixed with oil and surfactant; and (c) spent-acid and de-emulsifier is mixed with oil and surfactant.

These three systems were further analyzed by measuring the viscosity of the emulsion over time. The results over 5 days are shown in Figure 6 right after mixing, after 5 hrs., 1 day, 3 days, and 5 days. It shows that the presence of the surfactant in the oil, when mixed with spent-acid, results in a viscous emulsion that is almost ten times more viscous than the oil. The value of the viscosity drops to around 0.14 Pa.s (140 cp) after 24 hrs; however, it is still more than 5.4 times the oil's viscosity. The oil itself also produces a stable emulsion when mixed with the spent-acid. However, the viscosity starts at around 0.13 Pa.s (130 cp) then drops to around 0.06 Pa.s (60 cp), a little over two times the viscosity of the oil. The addition of the de-emulsifier to the spent-acid shows that it effectively limits the stability and viscosity of the emulsion in the presence of the surfactant; the complete separation between the spent-acid and the oil is observed by day 5; as confirmed in the image shared in Figure 5c. These results ensure that using these three systems in flooding tests can provide insight into emulsions' possible role during the process of oil flowback.

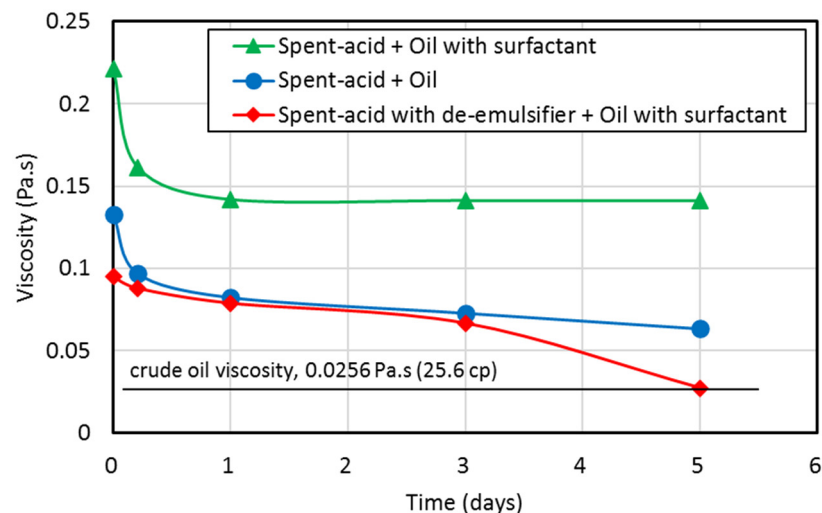


Figure 6. Spent-acid + Oil emulsion viscosity vs. time for the three scenarios.

3.3. Core Flooding Tests

The three fluid systems were utilized in the flooding experiments. This section compares and analyzes the pressure response from these scenarios during the three stages of injection.

The first graph, shared in Figure 7, shows the pressure response when the spent-acid is injected for the three scenarios. The lowest pressure was observed when the de-emulsifier was added to the spent-acid, which was associated with the case of a surfactant added to the oil. The pressure profile for the case of the two emulsion-prone systems shows a slope of pressure build-up that is double that of the emulsion-free system. Given that the only difference between the fluid systems is their susceptibility to emulsions, this could reveal that the injection of acid results in mixing, leading to the formation of emulsions and resulting in higher resistance to flow. While it is not the only mechanism that explains these results, it is evident that emulsion-prone systems have a very different flow behavior than emulsion-free systems.

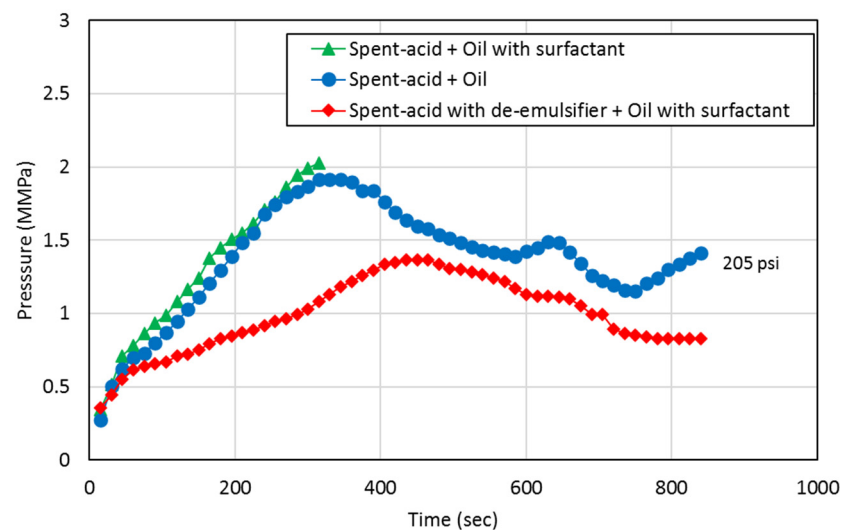


Figure 7. Pressure responses when spent-acid was injected for the three scenarios.

The result of pressure build-up when injecting oil from the outlet of the core following spent-acid injection is captured in Figure 8. In all three scenarios, the two-phase immiscible flow resulted in pressure values beyond the pressure transducer's limits. However, when a de-emulsifier is used, a slow pressure build-up was observed in the case of oil flow. Both oil injection cases without the use of a de-emulsifier recorded the fastest pressure build-up, indicating that oil is experiencing a higher resistance to flow. The presence of the surfactant in the oil results in a more accelerated pressure build-up as it intensifies the emulsion problem. The drop in the slope of pressure build-up by less than half when a de-emulsifier is used indicates that the effective permeability to oil has been doubled in the emulsion-free fluid system compared to the emulsion-prone systems. Oil flowback represents a cleanup mechanism that removes the spent acid and reaction products from the acidized region. The mechanism of acid-oil interactions that results in viscous emulsions negatively impacts the flow capacity for oil, reflecting the damage to well productivity resulting from emulsions when de-emulsifiers are not utilized. Given that many small operators elect to inject straight 15% HCl solutions into the wells without regard to additives such as de-emulsifiers, the results show the critical need to invest in such additives after identifying the suitable type and amount of de-emulsifier for the relevant fluid system.

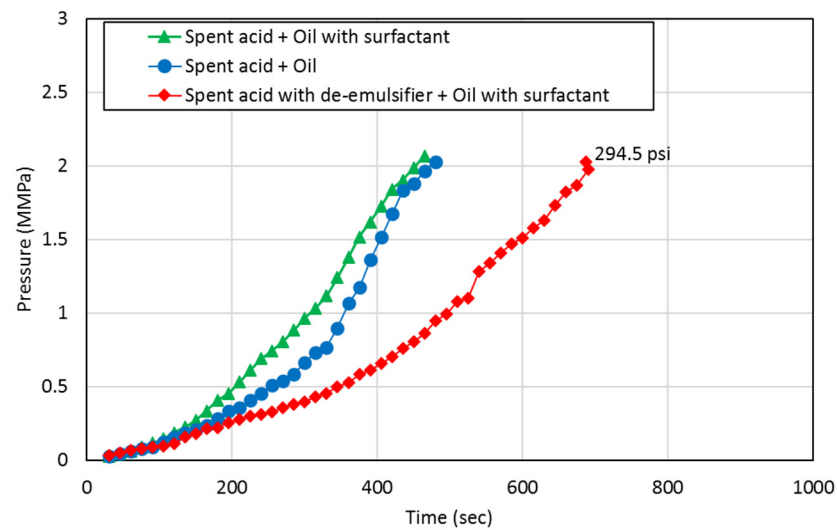


Figure 8. Pressure responses for the three scenarios when oil was injected from the outlet end of the core after spent-acid injection from the inlet side was completed.

Since the same core was used in these three flooding scenarios and had to undergo multiple rounds of cleaning in between the various stages, we compared the pressure building during oil injection before spent-acid was injected into the core to confirm that the core did not change and that the initial condition was reproduced in each experiment. Also, absolute permeability was measured after each cleaning, which was maintained at 55 mD. The results shared in Figure 9 show that the pressure profiles follow the same trend in all three cases. This shows that the alteration to the core properties was minimal during these rounds of injection and that the cleaning protocol was successful in establishing reproducibility.

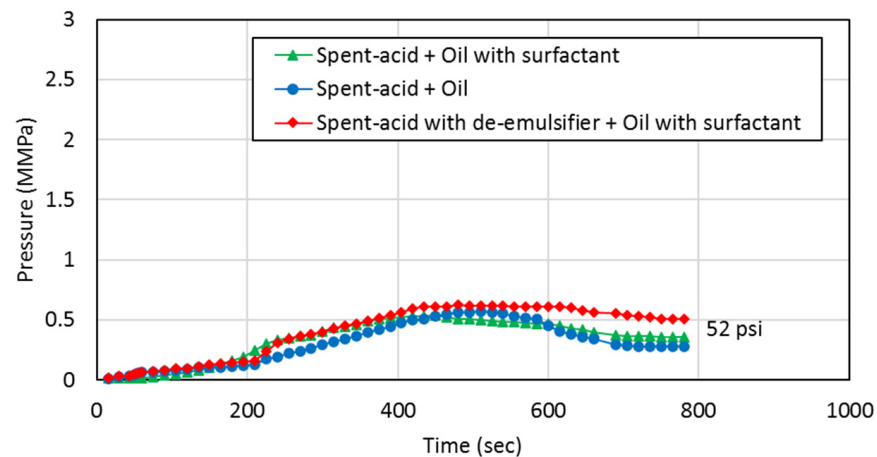


Figure 9. Pressure responses from the three scenarios when oil was injected at the inlet of the oil-saturated core before spent-acid was injected.

4. Conclusions

While many studies exist that study the process of matrix acidizing in laboratory settings, very few studies are relevant to the field conditions where the presence of oil results in conditions that can impact well productivity after stimulation. The following conclusions can be drawn from the results shared in this study:

- Emulsion-prone systems result in higher resistance to flow during both the acid injection phase and the oil production phase indicating reduced flow capacity in

the pore space, which can be explained by the presence of emulsions resulting from spent-acid and oil mixing.

- De-emulsifiers that successfully control the formation of emulsions result in doubling the flow capacity for both spent-acid and oil. This can improve the performance of the matrix acidizing treatment in carbonate formations.
- The experimental protocol followed in this study proved to be effective in documenting the de-emulsifiers' effect on flow properties in acidizing treatments.

Author Contributions: M.E. conducted all the experimental work and initial analysis, in addition to writing the initial draft of the paper. M.F. participated in the experimental design, analysis of the results, and finalizing the manuscript. C.T. contributed to the idea of simulating the wormhole through a drilled hole and assisted in the process of core preparations. All authors have read and agreed to the published version of the manuscript.

Funding: This research received no external funding.

Data Availability Statement: Not applicable.

Conflicts of Interest: The authors declare no conflict of interest.

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