RICE UNIVERSITY

Prevention and Control of Corrosion-Induced Asphaltene Deposition

by

Chi-An Sung

A THESIS SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE

Master of Science

APPROVED: THESIS COMMITTEE

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Francisco M. Vargas, Chair
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HOUSTON, TEXAS
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ABSTRACT

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Although in oil production multiple problems occur simultaneously, the solution strategy is typically presented by addressing one problem at a time. The objective of this thesis is to provide insight into the detrimental effect of iron ions, which are produced as a result of corrosion or contact with seawater in reservoirs, on the asphaltene precipitation and deposition tendency during asphaltene production. Furthermore, this work aims to provide means to control these adverse effects by using a chelating agent.

In a series of experiments, a model oil system, which was prepared by dissolving asphaltenes in toluene, was put in contact with aqueous solutions of iron ions to study the effect of these species on the stability of asphaltenes using the indirect method. In addition, other potential variables were included in this work to analyze their effects on asphaltene precipitation, such as the presence of emulsified water, salinity, acidic pH, and metallic ions valence. It was found that the solubility of iron species is relatively high in the oil phase, compared to other cations, and that unlike other variables has a significant destabilizing effect on the asphaltene system.

Also, a new experimental setup, consisting of a multi-section PTFE column packed with carbon steel spheres was built to quantify the deposition of asphaltenes
under different operating conditions. This device was used to study the effect of the aqueous iron solutions on the asphaltene deposition tendency. It was identified that iron ions in the bulk phase, iron oxide on metallic surfaces, and higher surface roughness potentially increase the tendency of asphaltene deposition. The correlation between the corrosion of pipelines and asphaltene deposition was determined in this work.

A chelating agent, Ethylenediaminetetraacetic acid (EDTA), was tried to reduce the detrimental effect of iron and successful results were obtained. It can be concluded that EDTA enables to restore asphaltene stability in the presence of iron ions.

According to the evidence obtained from this work, the corrosion of pipelines might be an aggravating cause for asphaltene deposition in wellbore and surface facilities. By addressing the corrosion problem, asphaltene deposition might actually subside.
The thesis would not have been possible without the help of so many people in so many ways during the last year and a half.

I would like to express my sincere gratitude to Dr. Francisco M. Vargas for his continuous support, criticism, encouragement and invaluable assistance throughout this study. His positive attitude and enthusiasm towards the work, knowledge and friendly nature were essential to my success here. I also appreciate his financial support throughout my graduate study.

I would also like to thank Dr. Walter G. Chapman and Dr. Scott Wellington for serving on my thesis committee and taking their time to review my thesis.

I would like to appreciate the patience and constructive feedback provided by Dr. Mohammad Tavakkoli. His extended help in experiments, expertise in petroleum engineering, and insights into the study really facilitated the completion of the work.

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Last but most importantly, I would like to deeply thank all my family members in Taiwan for their permanent love, confidence, and encouragement. If there was no support from them, I think it was not easy to determine to pursue further study in the United States and then persevere with the work.
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### Nomenclature

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<th>Description</th>
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<tr>
<td>ASD</td>
<td>Average Standard Deviation</td>
</tr>
<tr>
<td>EDDHA</td>
<td>Ethylenediamine-N,N'-bis</td>
</tr>
<tr>
<td>EDTA</td>
<td>Ethylenediaminetetraacetic acid</td>
</tr>
<tr>
<td>DTPA</td>
<td>Diethylenetriaminepentaacetic acid</td>
</tr>
<tr>
<td>HPHT</td>
<td>High Pressure High Temperature</td>
</tr>
<tr>
<td>NIR</td>
<td>Near Infared</td>
</tr>
<tr>
<td>PFA</td>
<td>Perfluoralkoxy</td>
</tr>
<tr>
<td>PTFE</td>
<td>Polytetrafluoroethylene</td>
</tr>
</tbody>
</table>
Chapter 1

Introduction

Understanding issues of asphaltene precipitation and deposition is of importance for the petroleum industry, as asphaltene precipitation and subsequent deposition constitute problems during oil production. Asphaltene deposition considerably affects the reservoir performance, such as the reduction of permeability and porosity, the alteration of wettability, as well as the plugging of wellbores and production equipment. The plugging would reduce oil flows in wellbores and pipelines, resulting in low efficiency of oil production. This phenomenon leads to significant costs. The cost of the lost production can be upwards of US $ 1 MM per day, and from the remediation, such as the removal of deposited materials, can be US $ 3 MM\(^1\). Therefore, the ability to understand and estimate the precipitation and deposition of asphaltenes in oils enables people to not only improve oil production but also save extra expenses for impairment of facilities and addition of inhibitors.
1.1. Research Motivation

It is generally known that asphaltene precipitation can arise from a myriad of factors, such as changes of surrounding pressure, temperature, and composition in reservoirs. Within the last few decades, several studies indicated that iron ions, coming from tubing corrosion or seawater, play a detrimental effect on reservoir performance. It has been recognized that the precipitation problem of asphaltenes can be aggravated by iron ions in several field analyses.²

Many pipelines used for oil transportation are made of carbon steel, and the corrosion of pipelines occurs in the presence of water, oxygen, or acidic components. Corrosion leads to the formation of iron oxide on the tubing wall and the variation of its surface roughness. Iron oxide or surface roughness affects the deposition of asphaltenes, and it is believed that they influence the deposition behavior of asphaltenes. However, the correlation between iron oxide and/or surface roughness and asphaltenes remains poorly understood, even though they are important parameters for asphaltene deposition.

To prevent the asphaltene deposition caused by corrosion, it is crucial to understand iron-induced precipitation since precipitation is the key step for the occurrence of deposition. To control iron-induced asphaltene precipitation, it is necessary to understand the interaction between iron ions and asphaltenes. Therefore, this study provides an insight into the effect of iron ions on asphaltene precipitation in the oil system.
Availability of field data on asphaltene deposition is very deficient, since obtaining such data is costly and time-consuming. Until now, various experimental setups have been developed to try to study asphaltene deposition in pipe flows, but there are still flaws in these techniques. Thus, an improved apparatus will be introduced in this work to probe the effect of corrosion on asphaltene deposition under dynamic conditions.

Various inhibitors have been employed to prevent the instability of asphaltenes in the crude oil. However, the problem of asphaltene instability caused by iron components remains challenging due to the undesirable performance of various inhibitors. In addition, few investigations focus on the mitigation of potential corrosion-induced asphaltene deposition problem. Accordingly, a novel method to stabilize asphaltenes in the presence of iron and corrosion is needed to develop.

1.2. Objectives

The followings are main objectives expected to achieve in this study.

1. Analyze the effect of iron ions on asphaltene precipitation in the oil system, and provide insight into the mechanism behind iron ions inducing the precipitation of asphaltenes.

2. Investigate the correlation between corrosion and asphaltene deposition under dynamic conditions, including effects of iron oxide and surface roughness on asphaltene deposition on metallic surfaces.
3. Mitigate the potential corrosion-related asphaltene deposition problem.

**1.3. Thesis Structure**

This thesis provides an overview of background for asphaltene and its impact on oil production. Especially asphaltene precipitation and deposition caused by corrosion are highlighted. The experimental procedure and apparatus used in the work are elaborated, followed by results and discussion. Finally, the conclusion and the future work are provided at the end of the thesis.

Chapter 2 offers an overview of oil characterization and the definition of asphaltenes. Additionally, Asphaltene precipitation and deposition is introduced, followed by the impact of these phenomena on oil production.

In Chapter 3, the impact of iron ions on the precipitation problem of asphaltenes in the oil is introduced. And then, the technique “Indirect Method” used to investigate the iron-induced asphaltene precipitation is elaborated, including the experimental procedure. Potential variables, such as the presence of emulsified water, salinity, acidic pH, and metallic ions valence are included into the analysis to study their effects on asphaltene precipitation. After that, the discussion is included.

In Chapter 4, an overview of corrosion of pipelines is offered, followed by its effect on asphaltene deposition. Further, a novel apparatus, which consists of multiple column sections, is introduced along with the experimental procedure. The effect of corrosion on asphaltene deposition is discussed in the following section.
Chapter 5 introduces the new method used to prevent the precipitation and deposition of asphaltenes caused by iron ions/corrosion. And then the result and discussion are presented.

Finally, in Chapter 6 conclusions and recommendations for the ongoing work are provided.
Chapter 2

Review of Asphaltenes in Crude Oils

This chapter provided the background of oil characterization, asphaltenes, and the impact of asphaltenes on oil production. The content includes an introduction to compositional analysis of crude oil, definition and properties of asphaltenes, and the problem arising from precipitation and deposition of asphaltenes during oil production.

2.1. Oil Characterization

Crude oil is a complex mixture, which contains a lot of components upwards of 100,000 molecules\(^3\). The predominant composition is hydrocarbons, additionally with other elements such as nitrogen, sulfur, and oxygen as well as metals\(^4\). Such complex structures make the analysis of the composition of crude oils considerably difficult. One technique developed by Jewell et al. is called the SARA analysis, broadly known to define the composition of crude oils\(^5\). The SARA analysis is
dividing the crude oil into saturate, aromatic, resin, and asphaltene (SARA) fractions depending on their solubility and polarity. The saturate fraction has nonpolar molecules including linear, branched, and cyclic saturated hydrocarbon. Aromatics consist of one or more aromatic rings, including benzene and the derivatives. The other two fractions, resins, and asphaltenes, contain polar substituents. Asphaltenes are insoluble in an excess of paraffinic solvents like heptane or pentane; however, resins are miscible with these solvents. The SARA analysis aids to classify the fractions of crude oils, in addition, to identify the potential problems from asphaltenes. Figure 2.1 elaborates a typical compositional analysis of a crude oil according to the SARA analysis.6

![Diagram of SARA analysis]

**Figure 2.1 – The schematic of classification for the SARA analysis.**

The SARA analysis is simple to be conducted in laboratories, but different analysis results can be obtained from different laboratory methods. Although one
crude oil can have two or more SARA results, this method is widely used to analyze the composition of crude oils due to its simplicity.

In SARA analysis, three main approaches were used to divided crude oils and other hydrocarbon molecules into SARA fractions. A clay-gel adsorption chromatography method, which is the basis of ASTM D2007, has two improved methods. First one is high pressure liquid chromatographic (HPLC) method, first introduced by Suatoni and Swab. HPLC techniques are faster, more reproducible than original ASTM technique, and able to separate heavier fractions from oils. However, in this case before chromatographic analysis, asphaltenes should be removed from other crude oil components to avoid adsorption or precipitation of asphaltenes during the elution step. Another separation method, using thin-layer chromatography (TLC) with flame ionization detection, was first applied by Suzuki and now is used extensively.

### 2.2. Definitions and Properties of Asphaltenes

The term, asphaltene, was originated in 1837 by J.B. Boussingault due to its asphalt-like properties. As mentioned in the last section, asphaltenes were found to be along with resins, aromatic hydrocarbons, and saturated hydrocarbons. Asphaltenes exert a significant influence on the physical properties of crude oils, such as high viscosity and specific gravity.

There is no specific standard to characterize asphaltenes. Several definitions of asphaltenes according to their appearance, solubility, molecular weight, and
structure are listed as follows. Speight\textsuperscript{11} stated that asphaltenes are dark brown to black friable solids. They do not have a definite melting point, and usually foam and swell while being heated. Speight also characterized asphaltenes based on the molecular weight, saying that asphaltenes are the most polar fraction in crude oils, with the molecular weight in the range of 400 to 1500 amu. Becker\textsuperscript{10} attempted to define asphaltenes based on their structure. He proposed that asphaltenes mainly consist of polyaromatic benzene with sulfur, nitrogen, and oxygen, attached to minor fractions, such as vanadium and nickel in porphyrin structures. The average composition of asphaltenes is fairly well-known, though they are very complex. Asphaltenes are composed of carbon and hydrogen in approximately 1:1.2 ratio, with a few percent of heteroatoms\textsuperscript{4}. In Figure 2.2 two hypothetical structures of asphaltene molecules are shown\textsuperscript{12,13}.

![Figure 2.2](image)

\textbf{Figure 2.2} – Proposed asphaltene structures for (a) 510C Residue of Venezuelan Crude\textsuperscript{12}, and (b) Maya crude (Mexico)\textsuperscript{13}.
Whereas, asphaltenes are currently defined in terms of their solubility, which is first proposed by Kilpatrick et al.\textsuperscript{14}. Asphaltenes are soluble in aromatic solvents, such as benzene, toluene or xylenes, yet insoluble in light paraffinic solvents, such as \textit{n}-heptane or \textit{n}-pentane. Since limited information could exactly define asphaltenes, asphaltenes are classified as a solubility class, rather than as a chemical class. Nevertheless, polydispersity of asphaltenes can cause some problems as using different analytical methods to separate asphaltenes. Asphaltenes precipitates obtained from using respectively \textit{n}-heptane and \textit{n}-pentane reveal different appearances, as shown in Figure 2.3. Figure 2.3 (a) illustrates asphaltenes separated by using \textit{n}-heptane, and (b) appears asphaltenes collected by using \textit{n}-pentane\textsuperscript{15}.

![Figure 2.3 – Asphaltenes obtained from the crude oil by being precipitated using (a) \textit{n}-heptane and (b) \textit{n}-pentane\textsuperscript{15}.](image)

(a) \textit{n}-C\textsubscript{7} asphaltenes  
(b) \textit{n}-C\textsubscript{5} asphaltenes
2.3. Impacts of Asphaltenes on Oil Production

Asphaltenes are termed as “the cholesterol of petroleum” by Kokal and Sayegh\textsuperscript{16}, since asphaltene deposition causes clogging in wellbores and pipelines, resulting in reduced oil flows as well as impaired production equipment. The plugging problem caused by asphaltene deposition leads to a loss of revenue, including the removal of asphaltene deposits and lost production. The reduction of asphaltene deposits in the tubing or wellbores costs approximately US $ 0.5-3 MM, and the loss of production can cost upwards of US $ 1 MM per day\textsuperscript{1}. Figure 2.4 shows asphaltene deposition in the pipeline.

![Asphaltene deposition clogging in the pipeline. Courtesy of A. Pomerantz, Schlumberger.](image)

Figure 2.4 – Asphaltene deposition clogging in the pipeline. Courtesy of A. Pomerantz, Schlumberger.

Studying the behavior of asphaltenes is of importance in the petroleum industry because asphaltene destabilization is a common problem arising from continuous changes of temperature, pressure, and oil composition. As the
thermodynamic equilibrium of asphaltenes is disturbed by above factors, they become unstable, and then precipitation and subsequent deposition likely appear.

Vargas et al.\textsuperscript{17} proposed a conceptual mechanism to describe asphaltene precipitation and aggregation. Figure 2.5 illustrates the mechanism of asphaltene precipitation, aggregation, and aging. Asphaltene precipitation produces the first asphaltene particles termed as “primary particles” with a size of a few hundred nanometers\textsuperscript{17}. These particles can deposit on the surface by diffusion, or grow into larger particles\textsuperscript{18}. The process of asphaltene aggregation has been experimentally demonstrated to be reversible, by dissolving insoluble asphaltenes in good solvents like toluene, or breaking large aggregates into small particles by ultrasonic waves\textsuperscript{19}. However, as asphaltenes further aggregate and eventually change their structures to form solid-like materials, re-dissolution of asphaltenes is not easily achieved. Therefore, inhibitors are used as asphaltene dispersants to decrease the amount of larger aggregates. However, some asphaltene dispersants could worsen the problem of asphaltene deposition\textsuperscript{20}. According to the competition between asphaltene aggregation and deposition, the increase of micro-aggregates of asphaltenes could promote asphaltene deposition\textsuperscript{20}. Also, the deposition model developed by Eskin et al.\textsuperscript{21} indicated that only submicron asphaltene particles could deposit on the wall. Tavakkoli et al.\textsuperscript{22} stated that after the onset of asphaltene precipitation, larger aggregated asphaltenes tend to pass through the surface by the flow rather than deposit because of convective transfer. Further, Hashemi Kiasari et al.\textsuperscript{23} also presented that more asphaltene precipitation decreases asphaltene deposition rate
since the deposition process is diffusion controlled. Thus, that is why some inhibitors cannot actually diminish asphaltene deposition but worsen it.

Figure 2.5 – The multistep mechanism for asphaltene precipitation, aggregation, and aging. Reversible processes are illustrated by dual green arrows\textsuperscript{17}. 
Chapter 3

Investigation of Iron-Induced Asphaltene Precipitation

3.1. Iron-Induced Asphaltene Precipitation

According to the information given by section 2.3, the problem caused by instability of asphaltenes is evidently detrimental to oil production. Thus, it is important to estimate the occurrence of asphaltene precipitation and understand the origin. Many oil pipelines are made of carbon steel. Salts like sodium chloride, or gases like hydrogen sulfide and carbon dioxide in reservoirs would deteriorate pipelines. Especially during the acidizing treatment, hydrochloric (HCl) and organic acids are used widely to improve productivity or injectivity in low permeability reservoirs. In case that iron ions can be derived from pipeline corrosion by acid contact and present in the bulk phase of the oil\textsuperscript{24}. Also, iron ions are present in the crude oil because of the contact with seawater in reservoirs. Figure 3.1 depicts the
corrosion process. In analyses of formation damage from several fields, the precipitation problem of asphaltenes has been found being aggravated in the presence of iron ions. Further, Fredd et al. mentioned that asphaltic sludge precipitation in a particular crude oil is induced by ferric ions rather than hydrogen ions from acid.

![Figure 3.1 - Schematic of corrosion cells on iron](image)

The correlation between iron and asphaltenes in crude oils has been recognized for a few decades. Nalwaya et al. stated iron increase the amount of polar components, such as asphaltenes, precipitated from oils. Studies during the bitumen extraction reported that insoluble organic molecules and undesirable emulsions are attributed to the iron content in oils. Although the mechanism of iron-induced asphaltene precipitation has not been confirmed, there are some theories to explain the phenomenon. Some theoretical studies indicated that high
aromaticity and heteroatoms in asphaltene structures increase attractions between iron ions and asphaltenes, as well as decrease the activation energy of an iron-asphaltene complex\textsuperscript{32}. Additionally, the iron-asphaltene complex is formed due to the coordination of iron ions with functional groups in asphaltenes, such as phenolic hydroxyl\textsuperscript{33,34}. Ferrous ions can also induce asphaltic sludge precipitation. Even though the extent is moderate compared to that caused by ferric ions, it is still more severe than acid alone\textsuperscript{35}. Although iron-induced asphaltene precipitation has been identified, more investigations are needed to understand how iron ions affect asphaltene precipitation.

### 3.2. Asphaltene Precipitation Tests

#### 3.2.1. Samples Preparation

Asphaltenes were extracted from crude oil $P$ using normal pentane as the precipitant and then were dissolved in toluene to prepare model oil systems. In the study of asphaltene precipitation, the model oil with 0.5 wt\% asphaltene concentration was used to prepare samples. 0.5 wt\% for the concentration of asphaltenes in the model oil represents a low asphaltene content, which is typical in light crude oils with a propensity to show asphaltene deposition problems in the field. Once the methodology is good enough for this low asphaltene content oil, it seems to work well for high asphaltene content oils, like crude oil $MY$ and crude oil $A$. For some of the indirect method experiments in this study, the water-in-oil emulsion is mixed with $n$-heptane during the sample preparation. Therefore, the
emulsion should be prepared prior to mix with $n$-heptane. The emulsion was prepared by slowly adding the desired amount of the aqueous phase (which could be deionized water or iron ions dissolved in deionized water) to the sample while the mixture was homogenized with a SCILOGEX D-160 homogenizer at approximately 20,000 rpm for 10 minutes. Deionized water was obtained from a Millipore Direct-Q3 water purification system.

3.2.2. Indirect Method

In this work, a recently developed technique called “Indirect Method” was used for determination of asphaltene precipitation. The schematic of the experimental procedure for the indirect method is illustrated in Figure 3.2. This method, which is a combination of gravimetric and spectroscopic techniques, has been proposed for the detection and quantification of asphaltene precipitation in dead oil samples. The term “indirect” refers to an indirect detection of the precipitation of asphaltenes by measuring the absorbance of the supernatant fluid after centrifugation of oil/$n$-alkane mixtures. More details of the indirect method procedure can be found in the literature. The indirect method was used in this study since it is more sensitive than other techniques that based on microscopy or direct spectroscopy. Also, it can be applied to detect asphaltene precipitation and quantify the amount that precipitates. By having a proper calibration curve, the absorbance of the supernatant fluid after the centrifugation step can be readily and accurately related to the amount of precipitated asphaltenes. Also, as part of this technique, all the aqueous phase can be separated by centrifugation and therefore
the absorbance of the supernatant liquid can be readily obtained, in the same way, it is done for an oil sample without the presence of an aqueous phase.

Figure 3.2 – Schematic of the indirect method procedure\textsuperscript{37}. 
In this study, all the experiments were conducted at 23 °C and at ambient pressure. In the indirect method, one set of experiment consists of 10 samples. Samples contain different ratios of model oil/emulsion and $n$-heptane, which are from pure model oil/emulsion to 90 vol% $n$-heptane, respectively. For the emulsion case, samples were stirred at 1150 rpm during the aging time to make sure that the aqueous and organic phases are mixed well. Aging time, which is the time allotted between sample preparation and centrifugation steps in the indirect method, is one day for all the indirect method experiments conducted in this study. After one day, the test tubes were centrifuged for 15 min at 10,000 rpm, which corresponds to 10,947 relative centrifuge force (RCF) in the Sorvall ST16 centrifuge. During the centrifugation step, asphaltene aggregates that are 100 nm and larger are settled. After centrifugation, the supernatant was taken and diluted with toluene and the absorbance value was measured at the wavelength of 700 nm, using the Shimadzu UV-3600 Spectrophotometer. More details on the indirect method experimental procedure, as well as the post-processing of the raw spectroscopy data, is available in the literature$^{36,37}$.

Every experiment presented in this study was repeated at least twice to ensure the repeatability of the experimental results. The average value of the results obtained is plotted in each figure, and the average standard deviation (ASD) is reported in the figure caption.
3.3. Analysis of Iron-Induced Asphaltene Precipitation

3.3.1. Effect of Fe (III) Ions on Asphaltene Precipitation

The indirect method was used to investigate the precipitation onset of the model oil with 0.5 wt% asphaltene concentration precipitated by \textit{n}-heptane. Samples were aged for one day at ambient conditions.

To analyze the effect of ferric ions on asphaltenes in the model oil system, a solution of Fe (III) ion was prepared by dissolving the anhydrous ferric chloride in deionized water. The concentration of the prepared Fe (III) ion solution was 2 wt%. As studying the effect of different concentration of Fe (III) ion solution, including 0.1, 0.2, 0.5, 1, and 2 wt%, on asphaltene precipitation, we found that the extent of asphaltene precipitation is proportional to Fe (III) ion concentration. To make sure that the effect of Fe (III) ions on asphaltene precipitation could be detected exactly, 2 wt% of Fe (III) ion concentration was selected in this work. The preparation of emulsion and experimental procedure were conducted as the same as the case of with emulsified water. Figure 3.3 compares results of the indirect method for the model oil diluted with \textit{n}-heptane and aged for 1 day, with and without the presence of Fe (III) ions.
Figure 3.3 – Results of the indirect method for the model oil with 0.5 wt% asphaltene concentration diluted with n-heptane and aged for 1 day at 23 °C and at ambient pressure, with and without the presence of emulsified Fe (III) ion solution. The ASD is 1.84% and 1.36% for no aqueous phase and 30 vol% Fe (III) ion solution, respectively.

Figure 3.3 compares results of the indirect method for the model oil with 0.5 wt% asphaltene concentration diluted with n-heptane and aged for 1 day, with and without the presence of Fe (III) ions. The onset of asphaltene precipitation for the case of without Fe (III) ion solution is between 40 and 50 vol% of added n-heptane. However, as Fe (III) ion solution was added in the system, the model oil is unstable from the beginning of the curve, i.e. 0 vol% of n-heptane. In case that we could not specifically define the onset of asphaltene precipitation. But a great drop in the absorbance values is between 30 and 40 vol% of added n-heptane. Furthermore, the absorbance values for the system of adding Fe (III) ions, the whole precipitation
curve noticeably deviates from the result without Fe (III) ion. According to this result, one may infer that before the great drop in the absorbance values, Fe (III) ions form a complex with asphaltenes in the organic phase even after the centrifugation, resulting in the increase of the absorbance values. With the increase of added \( n \)-heptane, Fe (III) ions might be more attracted to the precipitated and aggregated asphaltenes. Fe (III) ions get localized at or around the oil/water interface and also make more asphaltene aggregates adsorb to the interface. Hence, the absorbance values drop more in the presence of Fe (III) ions compared to the system without Fe (III) ions.

It is necessary to mention here that the increase of the absorbance values of the samples before the precipitation onset is not attributed to dissolution of iron ions in the organic phase. The experiment to analyze the solubility of Fe (III) ions in pure toluene and \( n \)-heptane was conducted by mixing toluene/\( n \)-heptane and Fe (III) ion solution for 1 day following the same experimental procedure. It was found that the absorbance of the supernatant after the centrifugation step is the same as the absorbance of pure toluene and pure \( n \)-heptane, and no increase was observed. Figure 3.4 and Figure 3.5 display the result for the solubility experiment. Therefore, Fe (III) ions do not dissolve in the organic phase during the indirect method experiments using the model oil system.
**Figure 3.4** – Absorbance values of emulsions of Fe (III) ion solution and pure toluene at different wavelengths using air as the blank.

**Figure 3.5** – Absorbance values of emulsions of Fe (III) ion solution and pure n-heptane at different wavelengths using air as the blank.
3.3.2. Effect of Emulsified Water on Asphaltene Precipitation

Water is inevitable in oil production, and just a trace amount of dissolved water can cause asphaltene self-association due to hydrogen bonding between heteroatoms of asphaltenes\textsuperscript{38,39}. Then, samples containing the emulsion of 30 vol\% water in oil was prepared and the experiment was conducted at the same condition. Deionized water was obtained from a Millipore Direct-Q3 water purification system. In case that the effect of emulsified water on the instability of asphaltenes can be studied. Figure 3.6 shows the results of the indirect method for the model oil with 0.5 wt\% asphaltene concentration diluted with $n$-heptane and aged for one day, with and without the presence of 30 vol\% emulsified water. Using the indirect method results, the first point which shows a deviation from the horizontal line represents the precipitation onset. In Figure 3.6, the onset point is between 40 and 50 vol\% of added $n$-heptane for both cases of with and without emulsified water. The result indicates that the presence of emulsified deionized water has no effect on the instability of asphaltenes extracted from crude oil $P$ in this work.
Figure 3.6 – Results of the indirect method for the model oil with 0.5 wt% asphaltene concentration diluted with \(n\)-heptane and aged for 1 day at 23 °C and at ambient pressure, with and without the presence of 30 vol% emulsified water. The ASD is 1.84% and 2.37% for no water and 30 vol%, respectively.

According to the study from Tavakkoli et al.\textsuperscript{37}, for some crude oils and model oil systems used in their study, emulsified water neither had a significant effect on the onset of asphaltene precipitation nor the amount of precipitated asphaltenes. However, some other systems were significantly affected by the presence of water. From their work, the effect of emulsified water on asphaltenes from different sources is related to the affinity of asphaltenes for the oil/water interface. They concluded that the heavier asphaltenes have more affinity for the oil/water interface\textsuperscript{37}. Also, other studies demonstrated that emulsified water does not affect the onset of asphaltene precipitation\textsuperscript{40,41}. 
3.3.3. Effect of Salinity on Asphaltenene Precipitation

The presence of emulsified water has no effect on asphaltene instability; however, the emulsified water was prepared by deionized water. In wellbores or pipelines, dissolved components in the crude oil, such as brine, would have an impact on asphaltene precipitation. To study the effect of salinity on asphaltene instability, sodium chloride solutions with the same pH value and conductivity value as Fe (III) ion solution was prepared to add in the model oil system. The pH value was adjusted by using hydrochloric acid (1.0 N) to reach 1.32, and the conductivity value, measured by using electrical conductivity meter, was 2756 μS/cm. The experimental procedure was the same as cases mentioned before. Figure 3.7 shows the effect of salinity on the instability of asphaltenes in the model oil system diluted with n-heptane and aged for 1 day. The onset shifts to the range between 30 and 40 vol% of added n-heptane. In addition, before the onset point, brine does not significantly affect the precipitation curve. After the precipitation onset, however, absorbance values drop more compared to the result of “No aqueous phase” case and incline to the absorbance values of the experiment with “30 vol% of Fe (III) ions solution.” The result for the presence of sodium ions is in line with the results presented by Tavakkoli et al. They stated that the presence of a brine solution in a crude oil system will cause a higher drop in the absorbance of the supernatant liquid after the onset of precipitation compared to the case of without presence of brine solution. Also, Serrano-Saldaña et al. and Alotaibi et al. concluded that the interfacial tension of n-C₁₂/brine interface decreases with increasing concentration of brine because ions from sodium chloride prefer to localize at or around the n-
C_{12}/brine interface. This might be the reason for the decrease in the absorbance of the supernatant liquid after the precipitation onset in the presence of brine solution compared to the experiment with no aqueous phase in the system.

![Graph showing absorbance at 700 nm vs. n-C₇ vol%](image)

Figure 3.7 – Results of the indirect method for the model oil with 0.5 wt% asphaltene concentration diluted with n-heptane and aged for 1 day at 23 °C and at ambient pressure, without the presence of an aqueous phase, with Fe (III) ion solution, and with Na ion solution. The ASD is 1.84%, 1.36% and 3.44% for no aqueous phase, 30 vol% Fe (III) ion solution, and 30 vol% Na ion solution, respectively.

### 3.3.4. Effect of Acidic pH on Asphaltene Precipitation

The addition of Fe (III) ions to deionized water changes the properties of the water. Acidic pH of the Fe (III) ion solution may affect the asphaltene instability. The pH value of the prepared Fe (III) ion solution in this work was 1.32. An acidic
solution with a pH value of 1.32 was prepared by mixing hydrochloric acid (1.0 \textit{N}) and deionized water. An emulsion was prepared using this acidic water and the model oil with 0.5 wt\% asphaltene concentration. The experimental procedure was the same as cases mentioned before. Figure 3.8 depicts results of the indirect method for the model oil diluted with \textit{n}-heptane and aged for 1 day, without the presence of water, with Fe (III) ion solution, and with acidic water. According to the result, low pH (acidity) of the solution does not change the precipitation curve before the onset point. However, after the precipitation onset, the absorbance values of the case of “30 vol\% of acidic water” fall between the values for the experiment with “30 vol\% of Fe (III) ions solution” and the experiment for “No aqueous phase.” Therefore, acidic pH of Fe (III) ion solution is responsible for a part of changes in the precipitation curve after the onset point.

From several analyses of fields, it is found that acid can induce asphaltene precipitation, resulting in severe plugging and formation damage in oil production facilities\textsuperscript{33,34,44}. It is believed that positively charged protons from acid neutralize asphaltenes and then larger aggregates of asphaltenes are formed\textsuperscript{24,45,46}. The extent of asphaltene precipitation can be augmented by the strength of the acid used. Therefore, acid is a crucial parameter to be taken into consideration for asphaltene precipitation.
Figure 3.8 – Results of the indirect method for the model oil with 0.5 wt% asphaltene concentration diluted with n-heptane and aged for 1 day at 23 °C and at ambient pressure, without the presence of an aqueous phase, with Fe (III) ion solution, and with acidic water. The ASD is 1.84%, 1.36% and 1.14% for no aqueous phase, 30 vol% Fe (III) ion solution, and 30 vol% acidic water, respectively.

### 3.3.5. Effect of Metallic Ions Valence on Asphaltene Precipitation

One may attribute the trivalence of Fe (III) ions to asphaltene instability. Thus, the effect of other trivalent metallic ions, such as Cr (III) ions and Al (III) ions, on asphaltene precipitation was studied here using the indirect method. Solutions of Cr (III) and Al (III) ions were prepared by dissolving chromium chloride hexahydrate and aluminum chloride in deionized water, respectively. Also, pH values for these two solutions were adjusted using hydrochloric acid (1.0 N) to reach the same pH value of the Fe (III) ion solution, i.e. 1.32. Conductivity values of
these metallic ion solutions were also the same as the Fe (III) ion solution, i.e. 2756 μS/cm. The experimental procedure was the same as cases mentioned before.

Figure 3.9 and Figure 3.10 show the effect of Cr (III) ions and Al (III) ions, respectively, on the instability of asphaltenes in the model oil system diluted with n-heptane and aged for 1 day. Although in the presence of Cr (III) ions the model oil is unstable from the beginning of the curve, the deviation of the absorbance values is minor compared to the system with Fe (III) ions. Al (III) ions do not significantly affect the onset of asphaltene precipitation. But for these two cases, with the increase of added n-heptane, absorbance values drop more compared to the result for the case of “No aqueous phase.” It could be caused by both acidic pH of the solution as well as metallic ions valence. In addition, the effect of Al (III) ions on asphaltene precipitation might be associated with the ion-bridging or chelating effect from Al (III) ions on heteroatoms of asphaltenes\(^\text{47}\). Further testing is necessary to verify the speculation.

Nevertheless, compared to the result of the addition of Fe (III) ions with such great deviation of the precipitation curve, it seems that the instability of asphaltenes is caused by Fe (III) ions alone due to the interaction between Fe (III) ions and asphaltenes. The phenomenon of asphaltene instability is not dominated by metallic ions valence.
Figure 3.9 – Results of the indirect method for the model oil with 0.5 wt% asphaltene concentration diluted with n-heptane and aged for 1 day at 23 °C and at ambient pressure, without the presence of an aqueous phase, with Fe (III) ion solution, and with Cr (III) ion solution. The ASD is 1.84%, 1.36% and 2.52% for no aqueous phase, 30 vol% Fe (III) ion solution, and 30 vol% Cr (III) ion solution, respectively.
Figure 3.10 – Results of the indirect method for the model oil with 0.5 wt% asphaltene concentration diluted with n-heptane and aged for 1 day at 23 °C and at ambient pressure, without the presence of an aqueous phase, with Fe (III) ion solution, and with Al (III) ion solution. The ASD is 1.84%, 1.36% and 3.47% for no aqueous phase, 30 vol% Fe (III) ion solution, and 30 vol% Al (III) ion solution, respectively.

3.3.6. Effect of Fe (II) Ions on Asphaltene Precipitation

From Figure 3.1, Fe (II) ions are initially dissolved into the environment and then are oxidized to Fe (III) ions. Thus, during oil production the effect of Fe (II) ions on asphaltene instability needs to be studied. Figure 3.11 compares precipitation curves obtained using the indirect method for the model oil system diluted with n-heptane and aged for 1 day, in the presence of Fe (II) ion and Fe (III) ion solutions. The solution of Fe (II) ions was prepared by dissolving Fe (II) chloride tetrahydrate in deionized water. It should be mentioned that the pH value and the conductivity
value of the Fe (II) ion solution were the same as the solution of Fe (III) ion, i.e. 1.32 and 2756 μS/cm, respectively. Also, the experimental procedure was the same as cases mentioned before.

Figure 3.11 – Results of the indirect method for the model oil with 0.5 wt% asphaltene concentration diluted with n-heptane and aged for 1 day at 23 °C and at ambient pressure, without the presence of an aqueous phase, with Fe (III) ion solution, and with Fe (II) ion solution. The ASD is 1.84%, 1.36% and 4.38% for no aqueous phase, 30 vol% Fe (III) ion solution, and 30 vol% Fe (II) ion solution, respectively.

From Figure 3.11, it can be concluded that the presence of Fe (II) ions does not significantly affect the precipitation curve before the onset point. However, after the precipitation onset, absorbance values drop more compared to the “No aqueous phase” case and are close to the absorbance values of the experiment with “30 vol%
of Fe (III) ions solution”. This drop is a result of both acidic pH of the solution and metallic ions valence. But it is obvious that the extent of asphaltene precipitation induced by Fe (III) ions is much more than that by Fe (II) ions. The result is consistent with the study proposed by Jacobs et al. It could be concluded that Fe (II) ions have fewer charges than Fe (III) ions, so the power of destabilizing asphaltenes is moderate than Fe (III) ions.
Det

etermination of Iron-Induced Asphaltene Deposition

4.1. Correlation between Corrosion and Asphaltene Deposition

Many oil pipelines are made of carbon steel exclusively. Salts like sodium chloride, or gases like hydrogen sulfide and carbon dioxide in reservoirs would deteriorate pipelines. According to Figure 3.1, rust formed by complex hydrates of iron oxide is produced and then accumulates on the wall of the tubing. Corrosion is one of the factors causing the threat in oil production and transmission in pipelines. Hazardous Materials Safety Administration (PHMSA) proposed that corrosion attributes to 18% of the significant incidents from pipelines between 1988-2008\textsuperscript{48}. NACE International (NACE) estimated all types of corrosion led to total costs up to US $ 276 billion\textsuperscript{48}. 
Several studies introduced the correlation between iron oxide and asphaltenes. In the compositional analysis of deposit materials, iron oxide was found significantly enriched in these deposits\textsuperscript{49}. In addition, the amount of asphaltenes adsorbed on iron minerals like hematite is significantly more than that on other minerals\textsuperscript{50}. Based on the study from Murgich et al.\textsuperscript{51}, low H/C ratio and heteroatom contents from asphaltenes could promote the adsorption on the iron oxide mineral. Further, the study from Wang et al. suggested that Fe (III) ions on the mineral surface are potential adsorption sites for polar components from the crude oil, such as asphaltenes, and then change the surface wettability\textsuperscript{52}. Although the adsorption and deposition of asphaltenes are not equivalent, these studies suggested that the interaction between asphaltenes and iron oxide. So iron oxide on the pipeline wall may affect the extent of asphaltene deposition. Further, iron ions are probably present in the crude oil because of the contact with seawater in reservoirs. Therefore, iron ions in the bulk phase of the crude oil could be taken into consideration for asphaltene deposition.

In general, corrosion produces isolated or linked pits on pipeline walls due to acidic environment. The pitting would roughen the surface of pipeline and cause fissures on walls, and then may increase the chance for asphaltenes depositing on. The variation of the surface roughness would affect the tendency of asphaltene deposition. Kiasari et al.\textsuperscript{23} used Quartz Crystal Nanobalance (QCN) method to investigate the effect of surface roughness on asphaltene deposition on stainless steel surfaces. They concluded that higher surface roughness facilitates higher asphaltene deposition rate, so using smoother stainless steel surfaces can mitigate
asphaltene deposition. As a result, the surface roughness is a parameter influencing asphaltene deposition. However, to the best of our knowledge, there is only one report in the literature introducing the effect of the surface roughness on asphaltene deposition\textsuperscript{23}. The correlation between corrosion and asphaltene deposition is not fully understood, even though corrosion is crucial to be taken into consideration for the prevention of asphaltene deposition.

**4.2. Previous Works for Studying Asphaltene Deposition**

Although predicting asphaltene precipitation is a key step in understanding asphaltene deposition, the two are not equivalent. The damage incurred is often due to the accumulation of the asphaltene deposits on the production tubing. However, availability of field data on asphaltene deposition is very limited, since obtaining such data is expensive and time-consuming. Thus, researchers have developed various experimental setups to study asphaltene deposition in pipe flows, such as metal capillary tubes, Couette devices, and Quartz Crystal Microbalance with Dissipation (QCM-D)\textsuperscript{53-55}. However, there are disadvantages associated with each technique. Metal capillary tubes are a popular and reliable method for studying asphaltene deposition, but it is difficult to find the deposition profile through the capillary tube and the length is also very large. Couette devices are costly and do not represent pipeline flow, which are typically Poiseuille flow, and mathematical modeling must be utilized to translate the results of the Couette device to pipeline flow. QCM-D is very sensitive, but it is mostly limited to the adsorption of asphaltenes. Studying asphaltene deposition with this method is not
straightforward as it is not easy to distinguish between adsorption and deposition with this method.

In the next section, a novel apparatus used to detect and quantify corrosion-induced asphaltene deposition under dynamic conditions is further elaborated.

4.3. Asphaltene Deposition Tests

4.3.1. Samples Preparation

The model oil system used here contains 5 wt% asphaltenes extracted from the crude oil \( P \). This concentration is considered as a high concentration compared to the model oil used for the indirect method tests, which had an asphaltene concentration of 0.5 wt%. This high concentration, i.e. 5 wt%, was used here in order to ensure stable emulsions during the experiment and to infuse enough amounts of asphaltenes into the deposition apparatus. Since current syringe pumps have the capacity up to 70 mL, the duration of the experiment should be extended. The current setup can be upgraded by using a couple of ISCO pumps to enlarge the oil volume infused into the column, and then it can be used for the oil with low asphaltene concentration. For some experiments in this study, the water-in-oil emulsion is mixed with \( n \)-heptane during the sample preparation. The preparation of emulsions is the same as mentioned in the indirect method.
4.3.2. Multi-Section Column System

A system based on a column packed with carbon steel spheres, depicted by Figure 4.1, was utilized to study asphaltene deposition on metallic surfaces. This setup was originally depicted by Favero et al.\textsuperscript{56} and improved by Melendez\textsuperscript{57}. The column section consists of a PTFE two-section column packed with low-carbon steel spheres, which compose the surface for which the asphaltenes can deposit on. The PTFE was chosen because the tendency of asphaltenes to form a deposit on PTFE is very low\textsuperscript{58}. In this case, the analysis of deposited asphaltenes is straightforward since the deposition will mainly form on the steel spheres. Spheres in two sections of the column were separated using a molded PTFE Mesh. The flow was driven through the column via PFA tubing at a constant flow rate using syringes (Hamilton Gaslight Syringes 100, 50, and 25 mL) and syringe pumps (Harvard Apparatus Pump 11 Elite and Chemyx Fusion 100).
Figure 4.1 – Schematic of the multi-section column system for asphaltene deposition tests\textsuperscript{57}.

The entire apparatus, including the syringe, the pump, the T-junction, and the column, is depicted in Figure 4.2. To conduct an experiment using the apparatus, one syringe is charged with oil/emulsion, and the other syringe is charged with the precipitant (\textit{n}-heptane was used in this study). Next, the syringes were programmed according to testing conditions, and the two pumps were started simultaneously. Once the pumps are turned on, the fluids flow down PFA tubing to the T-junction immersed in an ultrasonic bath (Branson 1800) at 40 Hz. The temperature was kept
at a temperature of 23 °C using a copper cooling coil connected to an external water bath. After mixing in the T-junction, the fluid would then flow from the bottom of the column (inlet) to the top of the column (outlet) and the effluent was collected for analysis. In case that an emulsion was used, a stir bar was placed in the syringe and the syringe was on top of a stirrer in order to ensure that the emulsion was well mixed at all times throughout testing. For the case that an emulsion was used, in order to ensure that the emulsion was well mixed at all times throughout testing, a magnetic stir bar was placed in the syringe and the syringe was on top of a stirrer.

Figure 4.2 – (a) Pumps and syringes. (b) T-junction and cooling coil. (c) Column sections in the asphaltene deposition apparatus.

At the end of each experiment, the column is drained by gravity and disassembled from top to bottom. After the device was disassembled, the
components and spheres were washed with toluene and the liquid was collected in separate containers. The solvent is then evaporated on a hot plate at 100 °C, and the mass of the asphaltenes deposited on the system can then be quantified.

This system offers several advantages over metal capillary systems. First, the column is packed with carbon steel spheres to increase the surface area for asphaltenes to deposit on, decreasing the necessary length of the tube to study deposition. As a result, this apparatus can study the effect of gravity on the system as well, whereas for metal capillaries the tube is often very long and cannot be installed vertically. Next, the apparatus consists of multiple column sections, so the deposition profile can be analyzed independently in this apparatus. Finally, the current apparatus operates at ambient temperature and pressure, but potential exists for a high-pressure and high-temperature system, as the apparatus can simply be constructed out of stainless steel parts rather than Teflon.

The experimental conditions reported in Table 4.1 were used in studying asphaltene deposition. Every experiment presented in this study was repeated at least twice to ensure the repeatability of the experimental results. The average value of the results obtained is plotted in each figure, and the corresponding standard deviation (ASD) is reported in the figure caption or in the table.
<table>
<thead>
<tr>
<th>Experimental Conditions</th>
<th>Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>Asphaltene concentration of the model oil</td>
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<tr>
<td>Oil/precipitant volume ratio</td>
<td>30/70</td>
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<tr>
<td>Duration of the experiment</td>
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</tr>
<tr>
<td>Flow rate</td>
<td>9 cm³/h</td>
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<tr>
<td>Temperature</td>
<td>23 °C</td>
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<tr>
<td>Pressure</td>
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<tr>
<td>Sphere radius</td>
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</tr>
<tr>
<td>Surface area of spheres packed in the column section</td>
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</tr>
<tr>
<td>Pore volume in the column section</td>
<td>5.60 cm³</td>
</tr>
</tbody>
</table>

Table 4.1 – Experimental conditions used for asphaltene deposition tests.

4.4. Analysis of Asphaltene Deposition on Metallic Surfaces

4.4.1. Asphaltene Deposition on Stainless Steel Surfaces

In this study, the model oil with 5 wt% asphaltene concentration was co-injected with \( n \)-heptane to see the amount of asphaltenes deposited on metallic spheres. Table 4.2 presents the amount of the asphaltenes deposited on spheres and
column, without the presence of an aqueous phase in the system. One can see from Table 4.2 that the amount of deposition on spheres in the bottom section is more than on spheres in the top section of the column. This means that the deposition rate is higher at the inlet of the column that is in line with some of the experimental data available in the literature obtained from the capillary tube tests\textsuperscript{55}.

<table>
<thead>
<tr>
<th></th>
<th>Spheres</th>
<th>PTFE Column</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Bottom</strong></td>
<td>17.4 ± 0.2</td>
<td>2.7 ± 0.1</td>
</tr>
<tr>
<td><strong>Top</strong></td>
<td>6.0 ± 1.2</td>
<td>0.9 ± 0.4</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td>23.4 ± 1.4</td>
<td>3.6 ± 0.5</td>
</tr>
</tbody>
</table>

**Table 4.2 – Amount of deposited asphaltenes on spheres and column in different sections without the presence of an aqueous phase.**

During the deposition experiment, a sample of the effluent was collected every one hour at the outlet of the column. This sample contains some precipitated asphaltenes particles, which didn't have a chance to deposit on spheres in the column. These asphaltenes are called asphaltenes sediments in this study. The collected effluent sample was then centrifuged to settle the asphaltenes sediments. The supernatant liquid was removed after the centrifugation and sediments were left on the hotplate to dry. The mass of the sediments was then measured and
reported for every injected pore volume during the experiment. Figure 4.3 shows the mass of aggregated asphaltenes in the outlet as the weight percent of the collected effluent per injected pore volume (injected P.V.), i.e. 1.61 cm$^3$. The diagram can indirectly indicate the amount of deposited materials on spheres with injected P.V. during the experiment. From Figure 4.3, the mass of aggregated asphaltenes shows an increasing trend with injected P.V. It means aggregated asphaltenes that enter the column at a later stage of the test have less chance to deposit on the spheres compared to the asphaltenes that enter the column sooner. Once the surface of spheres is covered with deposited asphaltenes, there is less chance for the asphaltenes that enter the column to deposit. Aggregated asphaltenes with no chance to deposit will pass through the column and then will be collected at the effluent. Figure 4.4 shows the asphaltene content as the ratio of infused asphaltene content (5 wt%) per injected P.V. without the presence of an aqueous phase. From Figure 4.4, in the beginning almost all of aggregated asphaltenes deposit on spheres but the amount gradually decreases. According to the study from Kurup et al.$^{59}$, the increase of deposits contributes to the decrease of the deposition rate on pipelines. As the deposit builds up, the flow velocity increases and then asphaltenes are pushed through the pipeline by convection. Tavakkoli et al.$^{22}$ also proposed that an increase in the flow rate reduces the deposition of asphaltenes on the stainless steel surface for a long time (at most 2.8 hours).
Figure 4.3 – Aggregated asphaltenes in the outlet as the weight percent of the collected effluent, without the presence of an aqueous phase in the system. The ASD is 1.01%.
4.4.2. Effect of Emulsified Water on Asphaltene Deposition

To investigate the effect of emulsified water on the deposition of asphaltenes in this system, water in oil emulsion was prepared by the model oil and deionized
water obtained from a Millipore Direct-Q3 water purification system. Table 4.3 presents the amount of deposited asphaltene on spheres and column, respectively with and without the presence of emulsified water. It can be seen that the amount of deposited asphaltene in the presence of emulsified water does not show a significant difference with the amount deposited once there is no aqueous phase in the system. Aslan et al.\textsuperscript{62} examined the effect of water on asphaltene deposition using the stainless steel tubing, and they concluded that water evidently delays asphaltene aggregation or deposition. Water interacts with heteroatoms (N, O, S) in asphaltene by hydrogen bonding, which may make asphaltene transfer from hydrophobic to hydrophilic states. The stainless steel surface is more hydrophobic\textsuperscript{62–64}, so in case that asphaltene deposition could be delayed by water. However, the same result cannot be inferred from Table 4.3. The amount of deposited asphaltene on spheres in the case of “With emulsified water” is a little bit more than the case of “No aqueous phase.”
Deposited asphaltenes, % of total infused asphaltenes

<table>
<thead>
<tr>
<th></th>
<th>No aqueous phase</th>
<th>With emulsified water</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Spheres</strong></td>
<td>23.4 ± 1.4</td>
<td>24.9 ± 1.5</td>
</tr>
<tr>
<td><strong>PTFE Column</strong></td>
<td>3.6 ± 0.5</td>
<td>0.8 ±0.1</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td>27.0 ± 1.9</td>
<td>25.7 ± 1.6</td>
</tr>
</tbody>
</table>

Table 4.3 – Amount of deposited materials on spheres and column in different systems, with and without the presence of emulsified water.

Figure 4.5 shows the mass of aggregated asphaltenes in the outlet as the weight percent of the collected effluent per injected P.V., with and without the presence of emulsified water. Also, from Figure 4.5, it could not be concluded that water delays the asphaltene deposition on the stainless steel surface.
Figure 4.5 – Aggregated asphaltenes in the outlet as the weight percent of the collected effluent, with and without the presence of emulsified water in the system. The ASD is 1.01% and 0.73% for no aqueous phase and with emulsified water, respectively.

4.4.3. Effect of Fe (III) ions on Asphaltene Deposition

To study the effect of ferric ions in the bulk phase of the oil on asphaltene deposition, the emulsion was prepared by the model oil and 2 wt% Fe (III) ion solution. Table 4.4 presents the amount of deposited materials on spheres and column, respectively without aqueous phase and with emulsified Fe (III) ion solution. The amount of deposited materials in the presence of emulsified Fe (III) ion solution is much higher than the case of “No aqueous phase.” This could be due to the presence of both asphaltenes and Fe (III) ions in the deposited materials. Fe
(III) ions have a high affinity for asphaltenes and form a complex with them. Then, this complex forms a deposited layer on the spheres.

<table>
<thead>
<tr>
<th>Deposited material, % of total infused asphaltenes</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>No aqueous phase</strong></td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td>Spheres</td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td>PTFE Column</td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td>Total</td>
</tr>
<tr>
<td></td>
</tr>
</tbody>
</table>

**Table 4.4 – Amount of deposited materials on spheres and column in different systems, without aqueous phase, and with emulsified Fe (III) ion solution.**

Figure 4.6 (a) and (b) show collected spheres with deposited materials after experiments, respectively in the system “No aqueous phase” and “With emulsified Fe (III) ion solution.” It can be observed brownish materials attached on spheres. The materials could be the Fe-asphaltene complexes. According to the study from Wang et al., Fe (III) ions could promote the increasing amount of deposition because of ion-bridging or chelating effect of Fe (III) ions acting on heteroatoms (O, N, S) from asphaltenes. Further, from their ICP analyses, Fe ion was found abundant in the deposit, indicating that the interaction between Fe ions and asphaltenes.
Figure 4.6 – Collected spheres with deposited materials after experiments, in the system of (a) no aqueous phase, and (b) with emulsified Fe (III) ion solution.

To know the mass of pure asphaltenes in deposits, spheres were washed with a mixture of toluene and EDTA solution. Pure toluene is not helpful here because Fe (III) ions may go to the organic phase and form a complex with asphaltenes as we have shown previously. Therefore, the EDTA solution is necessary to sequester Fe (III) ions from the organic phase because Fe (III) ions have a higher affinity to EDTA than asphaltenes. After washing spheres, the emulsion was centrifuged to separate the organic phase from the EDTA solution. The organic phase, which is made of dissolved asphaltenes in toluene, was then left on a hotplate. The mass of asphaltenes was measured after completing evaporation of toluene. The total mass of deposited asphaltenes was 20.7% of total infused asphaltenes, which is much lower than the mass of deposited materials in the presence of Fe (III) ion solution. While compared to cases “No aqueous phase” and
"With emulsified water," the amount of deposits asphaltenes in the presence of Fe (III) ions is almost the same.

It could be concluded that Fe (III) ions in the bulk phase stick to asphaltenes, and then the Fe-asphaltene complex undergoes an aggregation process. As mentioned in section 2.3, larger aggregates are not suitable to deposit on the surface\textsuperscript{21-23}. Thus, the amount of pure asphaltene deposition on spheres decreases in the case of “With emulsified Fe (III) ion solution.” However, the total amount of deposition on spheres significantly increases in the presence of Fe (III) ions. These deposited materials may stick firmly to metallic walls of production tubing and would be hard to remove; therefore, the plugging problem becomes severe by these iron-induced deposited materials in the tubing.

Figure 4.7 illustrates the mass of aggregated asphaltenes in the outlet as the weight percent of the collected effluent per injected P.V., without an aqueous phase and with emulsified Fe (III) ion solution. In the presence of Fe (III) ions, the amount of aggregated asphaltenes is significantly more than that of without the presence of Fe (III) ions. According to the mechanism of asphaltene deposition, aggregated asphaltenes do not tend to deposit.
Figure 4.7 – Aggregated asphaltenes in the outlet as the weight percent of the collected effluent, without an aqueous phase and with Fe (III) ion solution. The ASD is 1.01% and 5.21% for no aqueous phase and with emulsified Fe (III) ion solution, respectively.

4.4.4. Effect of Corrosion on Asphaltene Deposition

To imitate the environment of corroded pipelines or wellbores, carbon steel spheres were corroded in advance. The acidic solution used to corrode spheres was prepared by dissolving sodium chloride in deionized water. The pH value and the conductivity value are the same as Fe (III) ion solution used in the previous system, i.e. 1.32 and 2756 μS/cm. Exposure time in acidic solution is 6 hours. After completing the corrosion, spheres were rinsed by using deionized water and dried by using acetone, and then packed into the column. To analyze the effect of surface
roughness on asphaltene deposition, corroded spheres were washed by acidic water with the same pH value as the corrosive solution and ultrasonic waves for 5 minutes to remove rust on them completely. After that, spheres were also dried by using acetone. Figure 4.8 shows original spheres (before corrosion), corroded spheres (with rust), and spheres with higher surface roughness (without rust). Images were taken by using HIROX KH8700 3D Digital Microscope. The corrosion rate \( C_R \) for corroded spheres calculated from Equation 4.1 is \( 17.6 \text{ g cm}^{-2} \text{ hr}^{-1} \).

\[
C_R = \frac{8.76W}{Atd}
\]

**Equation 4.1 – The formula for calculation of corrosion rate.**

where the unit mmpy represents millimeters per year, \( W \) is the weight loss of spheres (mg), \( A \) is the exposure area in the acidic solution (cm²), \( t \) is the exposure time (6 hours), and \( d \) is the density of spheres (8.43 g cm⁻³).
Figure 4.8 – Spheres taken (a) before corrosion, (b) after corrosion, and (c) after the removal of rust.

For cases using original spheres and spheres with higher surface roughness (without rust), it is assumed that no further corrosion would occur during the experiment. Thus, deposited asphaltenes could be quantified directly by comparing the mass of spheres before and after the experiment. But, for the case of using corroded spheres (with rust), asphaltenes cannot be quantified like other two cases because of iron oxide (rust) on spheres. So an alternative calculation is used to
quantify the amount of deposited asphaltenes on metallic surfaces. The mathematical formula is elaborate in Appendix A.

Table 4.5 shows the amount of deposited asphaltenes on original spheres, corroded spheres (with rust), and spheres with higher surface roughness (without rust). It is evident that amounts of deposited asphaltenes quantified on corroded spheres (with rust) and spheres with higher surface roughness (without rust) are further more than that on original spheres. For the case of “Corroded surface (with rust),” the presence of iron oxide on the surface seems to facilitate the deposition of asphaltenes. It may conclude that low H/C ratio and heteroatom contents from asphaltenes could promote the adsorption on iron oxide\textsuperscript{51}, or Fe (III) ions on the mineral surface are potential adsorption sites for polar components from the crude oil, such as asphaltenes\textsuperscript{52}. Additionally, Tavakkoli et al.\textsuperscript{22} investigated the interaction between asphaltenes and pipeline materials, such as stainless steel and iron oxide. From their study, it is observed that the adsorption of asphaltenes on the iron oxide surface increases in the beginning, but for a long time it decreases. However, the adsorption on the stainless steel surface is higher than that on the iron oxide surface, which is reverse to the result obtained in this study. It is possible that the variation of surface roughness in this case also contributes to increasing asphaltene deposition.
<table>
<thead>
<tr>
<th></th>
<th>Original spheres</th>
<th>Corroded spheres (with rust)</th>
<th>Spheres with higher surface roughness (without rust)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Spheres</td>
<td>23.4 ± 1.4</td>
<td>33.3 ± 1.0</td>
<td>33.6 ± 1.5</td>
</tr>
</tbody>
</table>

Table 4.5 – Amount of deposited asphaltenes on original spheres, corroded spheres (with rust), and spheres with higher surface roughness (without rust).

Figure 4.9 illustrates deposited materials on spheres after disassembling column sections in three cases. Figure 4.9 (b) shows that great amounts of asphaltic sludge were produced and trapped between spheres. This asphaltic sludge was hard to be drained out of the column by gravity. It indicates that Fe (III) ions definitely induced asphaltene precipitation. Figure 4.10 illustrates the mass of aggregated asphaltenes in the outlet as the weight percent of the collected effluent per injected P.V., in cases using original spheres, corroded spheres (with rust), and spheres with higher surface roughness (without rust). For the case of “Corroded spheres (with rust),” the amount of aggregated asphaltenes is much lower compared to the case of “Original spheres.” It could be concluded that aggregated asphaltenes tended to deposit on corroded spheres and/or are trapped between spheres in the column.

For the case of “Spheres with higher surface roughness (without rust),” the amount of deposited asphaltenes increases much more compared to the case of
“Original spheres.” It could be concluded that higher surface roughness leads to more surface area for asphaltenes to deposit on, which is consistent with the study from Hashemi Kiasari et al.23.

Figure 4.9 – Deposited materials on spheres after disassembling column sections, respectively are (a) on original spheres, (b) on corroded spheres (with rust), (c) on spheres with higher surface roughness (without rust).
Figure 4.10 – Aggregated asphaltenes in the outlet as the weight percent of the collected effluent, in systems using original spheres, corroded spheres (with rust), and spheres with higher surface roughness (without rust). The ASD is 1.01%, 0.80%, and 0.89% for original spheres, corroded spheres, and spheres with higher surface roughness, respectively.
Chapter 5

Prevention of Iron-Induced Asphaltene Instability by Chelation Chemistry

According to the aforementioned fact about iron-induced asphaltene precipitation, iron ions have high affinity for asphaltenes, resulting in the formation of the iron-asphaltene complex. Asphaltenes tend to precipitate, aggregate or deposit, and eventually cause costly damage on oil production. To solve the potential problem caused by iron-induced asphaltene precipitation and deposition in the oil, the strategy is to avoid the interaction between asphaltenes and iron ions.
5.1. Challenges in Current Treatments of Iron-Induced Asphaltene Instability

Various inhibitors, such as anti-sludging agents, corrosion inhibitors, and iron-reducing agents, have been employed to prevent the instability problem of asphaltenes in the crude oil with the presence of iron components. However, the effectiveness of these additives is limited by poor knowledge in their interactions with crude oils, as well as the compatibility issue for the combination of additives. Some chemical additives, preforming as dispersants, can slow down asphaltene aggregation rate, but the performance of additives are different. Thus, the addition of dispersants is no guarantee of stable asphaltenes in the oil. Besides, dispersants somehow reversely aggravate the extent of asphaltene deposition. Therefore, the chelating agent, which is more cost-effective, is used to better control the adverse effect of iron components on asphaltene instability in the oil system.

5.2. Studies for Chelation of Dissolved Scale in Petroleum Industry

By the addition of the chelating agent, dissolved iron ions in crude oils can be sequestered and then form a highly stable complex with the chelating agent. In the petroleum industry, iron ions, which can aggravate the precipitation problem of asphaltenes, are derived from corrosion of pipelines during acidizing treatments. Several studies have used the chelating agent as an alternative treatment for formation damage in oils as a result of acid contact. The chelating agent can stabilize
the dissolved scale in oils, such as metallic ions, to prevent re-precipitation of asphaltenes\textsuperscript{26,68–70}.

5.3. Chelation Chemistry by Ethylenediaminetetraacetic acid (EDTA)

Ethylenediaminetetraacetic acid, abbreviated as EDTA, is a widely used chelating agent in industrial application, such as the removal of rust or metallic ions, due to its excellent chelating performance and low cost. Figure 5.1 shows the chemical structure of EDTA and the metal-EDTA complex\textsuperscript{71}.

![Chemical structure of EDTA and metal-EDTA complex](image)

Figure 5.1 – (a) Chemical structure of EDTA, and (b) the complex of EDTA and metallic ion\textsuperscript{71}.

The mechanism of EDTA chelation is related to the formation of metal-EDTA complex. EDTA appears as its fully ionized state by stepwise losing protons as shown in Equation 5.1\textsuperscript{26}. 
\[ H_4Y \rightleftharpoons H_3Y^- + H^+ \]
\[ H_3Y^- \rightleftharpoons H_2Y^{2-} + H^+ \]
\[ H_2Y^{2-} \rightleftharpoons HY^{3-} + H^+ \]
\[ HY^{3-} \rightleftharpoons Y^{4-} + H^+ \]

Equation 5.1 – EDTA undergoes a stepwise loss of protons to reach its fully ionized state\(^{26}\).

The fully ionized form \( Y^+ \) of EDTA contains sufficient bonding sites with the correct spacing to occupy all the metal ion coordination sites. The metal-EDTA complex forms as shown in Equation 5.2\(^{72}\).

\[ M^{n+} + Y^{4-} \rightleftharpoons [MY]^{(n-4)+} \]

Equation 5.2 – The formation of a metal-EDTA complex\(^{72}\).

where \([MY^{(n-4)+}]\) is the concentration of chelated metal, \([M^{n+}]\) is the concentration of unchelated metal, and \([Y^+]\) is the concentration of free fully protonated EDTA.

EDTA behaves strong affinity for sequestering metallic ions with high stability. The stability constant (K), obtained from the equilibrium of metallic ion and EDTA, indicates how stable the metal-EDTA complex behaves, and the formula is shown in Equation 5.3\(^{72}\). The larger the stability constant is, the firmer the metallic ions are chelated by EDTA. Stability constants for various metal chelates of EDTA are listed in Table 5.1\(^{72}\).
\[ K = \frac{[MY]^{(n-4)+}}{[M^{n+}][Y^{4-}]} \]

**Equation 5.3 – The stability constant for the metal chelate of EDTA**

From Table 5.1, it can be observed that EDTA could definitely chelate iron ions with high stability.

<table>
<thead>
<tr>
<th>Metallic Ions</th>
<th>Log$_{10}$K</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe$^{3+}$</td>
<td>25.1</td>
</tr>
<tr>
<td>Fe$^{2+}$</td>
<td>14.3</td>
</tr>
<tr>
<td>Mn$^{2+}$</td>
<td>13.8</td>
</tr>
<tr>
<td>Ca$^{2+}$</td>
<td>10.7</td>
</tr>
<tr>
<td>Na$^+$</td>
<td>1.7</td>
</tr>
</tbody>
</table>

**Table 5.1 – Stability constants of various metal-EDTA chelates**

The pH value is a crucial factor for the chelation of EDTA. At low pH, protons would compete with metallic ions for free ionized EDTA, and then results in the less-ionized form that is poor-behaved in chelating metallic ions. Although the content of free ionized EDTA increases with pH values, hydroxide ions from the base may react with metallic ions to produce insoluble hydroxides. Accordingly, the pH value of EDTA solution used in this work was approximately 9.5 to make sure the
stability of the oil system. In the future work, we will work on acidic pH with other chelating agents without the formation of precipitation.

5.4. Mitigation of Iron-Induced Asphaltene Instability Using Ethylenediaminetetraacetic Acid (EDTA)

5.4.1. Mitigation of Asphaltene Precipitation under Static Conditions

In this work, EDTA solution was prepared by dissolving the reagent grade disodium salt dihydrate of EDTA in deionized water. The time frame for the entire experiment was 3 days. Emulsions of the model oil and Fe (III) ion solution were prepared and stirred for 24 hours on the first day. During the first step, Fe (III) ions and asphaltenes would form a complex in the oil system. On the second day, EDTA solution was added to the samples and stirred for 24 hours. In this step, it can be determined how powerful EDTA can be on sequestering Fe (III) ions from asphaltenes in the organic phase. On the third day, n-heptane was added to samples and stirred for 24 hours. After the third day, the test tubes were centrifuged and the absorbance of the supernatant was measured by means of the spectrophotometer.

Figure 5.2 illustrates results of the indirect method for the model oil diluted with n-heptane and aged for 1 day, without the presence of an aqueous phase, with Fe (III) ion solution, and with Fe (III) ion + EDTA solution.
Figure 5.2 – Results of the indirect method for the model oil with 0.5 wt% asphaltene concentration diluted with \( n \)-heptane and aged for 1 day at ambient conditions, without the presence of an aqueous phase, with Fe (III) ion solution, and with Fe (III) ion + EDTA solution. The ASD is 1.84%, 1.36% and 2.41% for no aqueous phase, Fe (III) ion solution, and Fe (III) ion + EDTA solution, respectively.

It can be concluded from Figure 5.2 that the addition of the EDTA solution could successfully capture the Fe (III) ions from the organic phase. The absorbance values before the onset point in the presence of EDTA are similar to the absorbance values of the case of “No aqueous phase.” Also, in the presence of the EDTA solution, the detection of asphaltene precipitation in the model oil system is very close to the system with “No aqueous phase,” which is between 40 and 50 vol% of added \( n \)-heptane (compared to the case of “With Fe (III) ions solution,” which is probably between 30 and 40 vol% of added \( n \)-heptane). Less precipitation happens exactly
before the onset in the presence of EDTA, but after the onset the stability of asphaltenes is not restored as the case of “No aqueous phase.” Before the onset (with less precipitant in the oil system), Fe (III) ions are chelated by EDTA and then have less chance to interact with asphaltenes, so the stability of asphaltenes in the oil system is not changed by Fe (III) ions. However, after the onset with more precipitant in the oil system, more asphaltenes precipitate and aggregate into larger particles, which may have stronger attractions with Fe (III) ions. It seems that there is the competition between asphaltenes and EDTA for Fe (III) ions, so some asphaltenes are still destabilized by Fe (III) ions and then get localized on or around the oil/water interface regardless of the presence of EDTA. While based on the results presented in Figure 5.2, Fe (III) has more affinity to form a complex with EDTA than asphaltenes in the system. Accordingly, EDTA can avoid the interaction between ferric ions and asphaltenes, and then prevent iron-induced asphaltene precipitation in the oil system. It can be expected that EDTA would reduce iron-induced asphaltene deposition.

Also, to understand whether EDTA reacts with asphaltenes in the model oil system, we conducted the indirect method for the model oil diluted with n-heptane with EDTA solution, and the result is shown in Figure 5.3. There is no significant deviation in absorbance values between two cases with and without the presence of EDTA. Hence, EDTA has no effect on asphaltenes and does not dissolve in the organic phase.
Figure 5.3 – Results of the indirect method for the model oil with 0.5 wt% asphaltene concentration diluted with n-heptane and aged for 1 day at 23 °C and at ambient pressure, with and without EDTA solution.

5.4.2. Mitigation of Asphaltene Deposition under Dynamic Conditions

To study the effectiveness of EDTA on the mitigation of iron-induced asphaltene deposition on metallic surfaces, the emulsion of the model oil, Fe (III) ion solution, and EDTA solution was prepared, and then charged into the column system with n-heptane. From Table 5.2, in the presence of Fe (III) ion and EDTA, the amount of deposited asphaltenes on spheres is 7.6% of total infused asphaltenes. In addition, from Figure 5.4 (b), the amount of deposits on spheres with the addition of EDTA is obviously less compared to (a) no aqueous phase. Caution that collected
deposits on spheres and column were washed by toluene and EDTA solution in the same procedure mentioned in section 4.4.3 to acquire pure deposited asphaltenes.

<table>
<thead>
<tr>
<th>Deposited asphaltenes, % of total infused asphaltenes</th>
</tr>
</thead>
<tbody>
<tr>
<td>No aqueous phase</td>
</tr>
<tr>
<td>------------------</td>
</tr>
<tr>
<td>Spheres</td>
</tr>
<tr>
<td>Column</td>
</tr>
<tr>
<td>Total</td>
</tr>
</tbody>
</table>

Table 5.2 – Amount of deposited asphaltenes on spheres and column in different systems, without the presence of aqueous phase, with emulsified Fe (III) ion solution, and with emulsified Fe (III) ion + EDTA solution.
Figure 5.4 - Collected spheres with deposited materials after experiments, in the system of (a) no aqueous phase, and (b) with emulsified Fe (III) ion + EDTA solution.

EDTA can stabilize Fe (III) ions by chelation, resulting in the decrease of asphaltene precipitation and aggregation. In addition, due to the affinity of asphaltenes for Fe (III) ions, asphaltenes could bond with Fe-EDTA chelates, resulting in larger complexes. This larger particle tends to be carried by the flow due to convective transfer, instead of depositing on spheres. Figure 5.5 displays the mass of aggregated asphaltenes in the outlet as the weight percent of the collected effluent per injected P.V., without an aqueous phase, with emulsified Fe (III) ion solution, and with Fe (III) ion + EDTA solution. From Figure 5.5, the amount of aggregated asphaltenes for the case of with EDTA is less than the case of without EDTA. It indicates that EDTA can mitigate the tendency of asphaltene aggregation in the presence of Fe (III) ions, which is consistent with the result of the indirect method shown in section 5.4.1.
In addition, from Table 5.2 it seems that aggregated asphaltenes prefer to attach on the PTFE column instead of spheres. However, to the best of our knowledge, asphaltenes do not tend to deposit on the PTFE material. It might be supposed that asphaltenes are led by the Fe-EDTA complex and/or EDTA because of attractions between them. There might be some problems arising from the compatibility of different strategies. Recently using PTFE coated tubing for oil production is being pursued by the industry. Nevertheless, once EDTA is used to mitigate the instability of asphaltenes caused by Fe (III) ions, the deposition problem on PTFE coated tubing should be concerned.
Figure 5.5 – Aggregated asphaltenes in the outlet as the weight percent of the collected effluent, without an aqueous phase, with Fe (III) ion solution, and with Fe (III) ion + EDTA solution. The ASD is 1.01%, 5.21%, and 4.48% for no aqueous phase, with Fe (III) ion solution, and with Fe (III) ion + EDTA solution, respectively.
Conclusions and Recommendations

6.1. Conclusions

In this thesis, iron ions, which are produced as a result of pipeline corrosion during oil production, have been identified to aggravate asphaltene precipitation in the model oil system. It could be concluded that Fe (III) ions have a high affinity for asphaltenes and form a complex with them. Thus, Fe (III) can destabilize asphaltenes and change the instability of asphaltenes in the oil. The analysis of effects of potential variables, such as the presence of emulsified water, salinity, acidic pH, and metallic ions valence, on asphaltene precipitation, indicated that Fe (III) ions alone in the oil could significantly destabilize asphaltenes. Fe (II) ions would destabilize asphaltenes, but its effect is not as significant as Fe (III) ions.

Asphaltene deposition under dynamic conditions was studied by using a PTFE multi-section column system packed with low-carbon steel spheres. It was
found that in the presence of Fe (III) in the bulk phase of the oil, deposited materials on metallic surfaces increased due to the ion-bridging effect of Fe (III) ions on heteroatoms of asphaltenes. However, the amount of deposited asphaltenes after removing Fe (III) ion content in the deposit decreased reversely. It was concluded that since Fe (III) ions and asphaltenes combined into larger aggregates, and these larger particles tended to pass through the surface by convection of the flow instead of deposition.

To study the effect of pipeline corrosion on asphaltene deposition, corroded spheres were prepared and then replaced original spheres put into the column. Corroded spheres with rust and without rust were used to study the effect of iron oxide components and surface roughness respectively on asphaltene deposition. It was found that iron oxide components on surfaces could increase asphaltene deposition, indicating that functional groups and heteroatoms from asphaltenes may facilitate the deposition on the iron oxide surface. Also, higher surface roughness increased asphaltene deposition on the surface. Consequently, corrosion is an important parameter to be taken into consideration for asphaltene deposition on metallic surfaces.

Ethylene diamine tetraacetic Acid (EDTA) was used to better control the adverse effect of iron on asphaltene precipitation and deposition. From the result of the indirect method, EDTA successfully restored the stability of asphaltenes in the presence of Fe (III) ions. In the asphaltene deposition test, EDTA reduced the amount of asphaltene deposition on metallic surfaces. Since EDTA chelates Fe (III)
ions in the oil and prevents the interaction between Fe (III) ions and asphaltenes, the extent of asphaltene precipitation could be mitigated. In addition, EDTA reduced asphaltene deposition on metallic surfaces. It may be attributed to the attraction of asphaltenes to Fe (III) ions, resulting in larger aggregates of asphaltenes and Fe-EDTA complexes formed. These bigger particles were not suitable to deposit on metallic surfaces. Nevertheless, EDTA might increase asphaltene deposition on the wall of a PTFE coated tubing. In conclusion, EDTA is a good choice to mitigate the tendency of iron-induced asphaltene precipitation, as well as reduce asphaltene deposition in the presence of iron ions.

6.2. Recommendations

According to the desirable result that EDTA better control asphaltene deposition in the presence of iron ions, it can be expected that EDTA would mitigate the extent of asphaltene deposition on corroded surfaces with iron oxide and higher surface roughness. Also, it is necessary to investigate the effect of corrosion and other potential variables on asphaltene in different crude oils.

Other chelating agents, like citric acid and phosphoric acid, were used in the indirect method to attempt to mitigate iron-induced asphaltene precipitation; however, the effectiveness was not good. Other chelating agents, such as DTPA or EDDHA, which have higher stability constants with iron ions, i.e. 28.0 and 35.4, respectively, could be studied in the future work.
The multi-section column system used to study asphaltene deposition can be further improved by using higher capacity pumps to allow larger infused oil volume into the column system. It can work on oils with lower asphaltene content and save time. Also, the setup can be implemented for HPHT conditions by replacing the PTFE column with a stainless steel one. Using a couple of ISCO pumps can allow higher pressure up to 5000 psi, and the column can be located inside a Blue M Electric oven to increase the temperature up to 250°F equivalent to 1232°C.

To obviate the suspicion of used PTFE column affecting asphaltene deposition, experiments by using new PTFE column would be conducted to see if the PTFE column is completely clean after the quantification of asphaltene deposition by washing with toluene.

According to the increase of asphaltene deposition on the PTFE column in the presence of EDTA, the effect of electrostatic charges on the PTFE column is one of potential factors. We are planning to remove electrostatic charges on the PTFE column to see if asphaltene deposition is still detected on the column.
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Appendix A. The Calculation to Quantify the Amount of Asphaltene Deposition on Corroded Spheres

In this section, the calculation to quantify the amount of deposited asphaltenes on corroded spheres (with rust) is elaborated. As mentioned in section 4.4.1, deposited asphaltenes could not be quantified directly by comparing the mass of spheres before and after the experiment because iron oxide components (rust) were also on spheres. So the mass of deposited asphaltenes on spheres was determined by using another procedure and calculation. The mathematical formula is shown as follows.

\[ m_1 = \text{the mass of corroded spheres} \]
\[ m_2 = \text{the mass of spheres with deposited materials} \]
\[ m_3 = \text{the mass of spheres with remaining rust} \]
\[ m_4 = \text{the mass of spheres without any rust} \]
\[ m_1 - m_4 = \text{the mass of rust on spheres} = m_5 \]
\[ m_2 - m_5 = \text{the mass of deposited asphaltenes} = m_6 \]

Equation A.1 – The formula for the quantification of asphaltene deposition on corroded spheres (with rust).

From Equation A.1, \( m_1 \) is the mass of spheres after corrosion, \( m_2 \) is the mass of spheres with deposited materials (asphaltenes and rust) after the experiment, and \( m_3 \) is the mass of spheres after removing deposited asphaltenes and part of rust on spheres by using toluene and ultrasonic waves. In this step, asphaltenes were
dissolved in toluene, including some iron components. After that, the remaining rust on spheres was removed by washing with the acidic water and ultrasonic waves for 5 minutes. The acidic water was prepared by the addition of hydrochloric acid in deionized water, and the pH value was 1.32, the same as the acidic solution used to corrode spheres. The mass of these spheres without any rust is m4. The difference between m1 and m4 is the mass of rust on spheres. Therefore, the mass of deposited asphaltenes on spheres could be obtained. Notice that the process to remove asphaltenes and rust on spheres should be quick in order to avoid further corrosion.