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Asphaltene, Naphthenic Acid and Naphthenate Components of Some Crude Oil Samples and Their Impact on Production and Export

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Highlights

- The Asphaltene and metal naphthenate components of crude oil samples from ten different wells within an oil reservoir were determined using different analytical techniques.
- The asphaltene content was determined by gravimetric analyses while the metal naphthenate components were determined by obtaining the metal ion concentration of the produced water and the naphthenic acid concentration of the crude using atomic absorption spectrometer (AAS) and potentiometric titration respectively
- All the crude samples possess asphaltene components as well as the propensity to form calcium and sodium naphthenate scale deposits
- The formation of naphthenate scale deposits is highly dependent on the pH of the produced water of the crude
- Both asphaltene and naphthenate deposits are directly proportional to the specific gravity of the crude and inversely proportional to the API gravity implying that both components reduce the quality of the crude.

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Abstract

The Asphaltene and metal naphthenate components of crude oil samples from ten different wells within an oil reservoir were determined using different analytical techniques. The asphaltene content of the crude was determined by gravimetric analyses using American Standard for Testing and Material (ASTMD 6560) to obtain its weight concentration while the metal naphthenate components were determined by obtaining the metal ion concentration of the produced water and the naphthenic acid concentration of the crude using atomic absorption spectrometer (AAS) and potentiometric titration respectively. Results obtained showed that the asphaltene content of the crude samples ranges from 2.0000 – 8.000 %w while the naphthenic acid concentration indicated by the total acid number (TAN) ranges from 0.3000 – 1.4600 mg/KOH/g. All the crude samples possess asphaltene components as well as the propensity to form calcium and sodium naphthenate scale deposits having a $Ca2+$ concentration between 32.5000 – 94.5000 mg/L and a $Na+$ concentration between 27.7 – 105.1 mg/L respectively, however the formation of naphthenate scale deposits is highly dependent on the pH of the produced water of the crude which makes well FT01 less likely to form naphthenate scales since it has a pH < 6, in other words, the produced water pH and availability of cations play an important role in the formation of naphthenate scales. Calcium naphthenate scale formation is more favored at brine pH > 6 while sodium scale formation is favored at a pH of approximately 8.5.

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Increase in produced water pH during crude oil production are usually caused during depressurization and release of CO_2. Both asphaltene and naphthenate deposits are directly proportional to the specific gravity of the crude and inversely proportional to the API gravity implying that both components reduce the quality of the crude. Asphaltene and metal naphthenate solid deposits in the crude can cause a lot of flow assurance difficulties such as, blocking of expedition lines, pore plugging, wettability, crude oil parameter alteration, as well as reduction in oil recovery.

Keywords: Expedition line, Flocculation, Flow assurance, Precipitation, Reservoir, Scale deposits.

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1. Introduction

The composition and characteristics of crude oil have a great deal of impact on its production, storage, transportation and export. A lot of processes and production equipment are affected by the quality of crude produced hence an in-depth knowledge of the components of the produced crude is essential in a lot of decision making in crude oil production ranging from choice of treatment chemicals, enhanced production techniques, process parameter adjustments and environmental impact assessment (Bai et al., 2010; Bartelli et al., 2014). The components of crude oil can be divided into several compounds and subdivisions based on the characteristics of the crude. Crude oil samples contain various percentages of dissolved gasses, liquids and solids, the liquids in crude oil can be subdivided into saturates, aromatics and resins (Sherif et al., 2010). Several forms of solids may exist in crude oil however the most prominent are the solid asphaltene and naphthenate deposits (Nicolas et al., 2014).

Asphaltenes are considered the most complex components of crude oil due to the complexity of their structure, all the liquid components of crude oil (saturates, aromatics and resins) have a general structure by which they are classified while asphaltenes have many different structures thereby making its generalization into a specific family very difficult (Ahmadi, 2011; Alrashidi et al., 2018). Several models have described the structure and characteristics of asphaltene however it is important to note that asphaltene is a solid phase homogenized in the crude at reservoir conditions (Zendehboudi et al., 2018). Figures 1, 2 and 3 show three different structures of asphaltene based on Archipelago, Continental and Yen-Mullins models respectively. Asphaltene is the highest molecular weight component in the crude that is insoluble in light n-alkanes such as n-pentane or n-heptane and soluble in aromatics such as toluene or xylene, it is highly polar and is associated with heteroatoms such as nitrogen, oxygen and Sulphur (Goual and Abudu, 2009). Asphaltene can cause a lot of problems to reservoirs because of its ability to form dense flocculation and deposits in wellbores of reservoir as well as transportation pipelines thereby resulting in serious operational and production challenges (Alrashidi et al., 2018). The behavior of asphaltenes vary with reservoir conditions hence understanding asphaltene behavior in the reservoir is critical in oil recovery as well as in asphaltene treatment (Ahmadi, 2011).

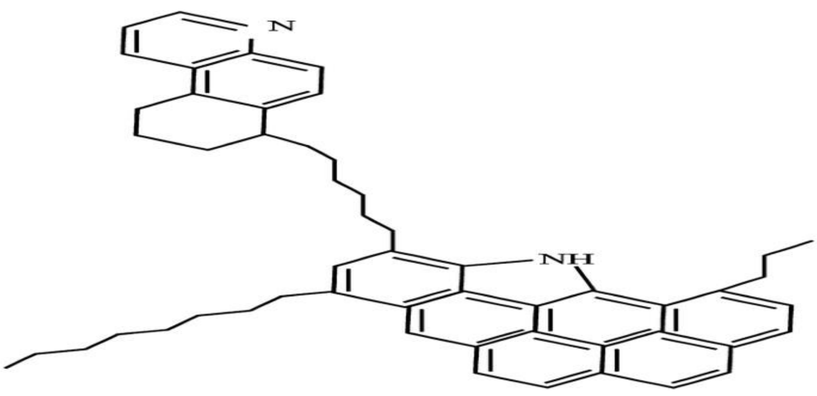

Figure 1
Archipelago asphaltene structure (Alvarez-Ramirez and Ruiz-Morales, 2003)

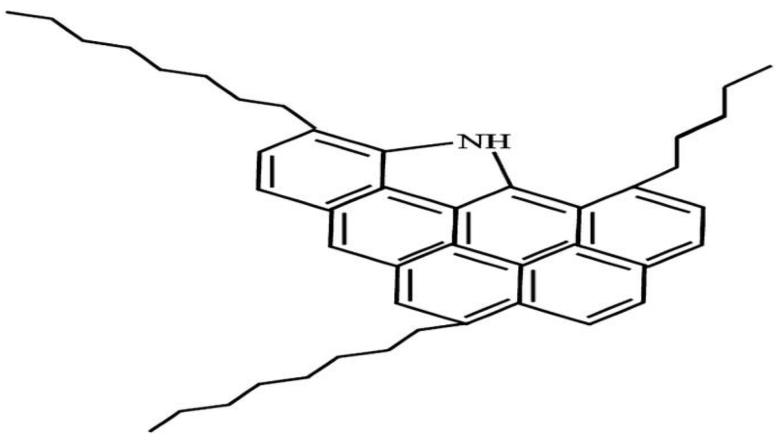

Figure 2
Continental asphaltene structure (Kuznicki et al., 2008)

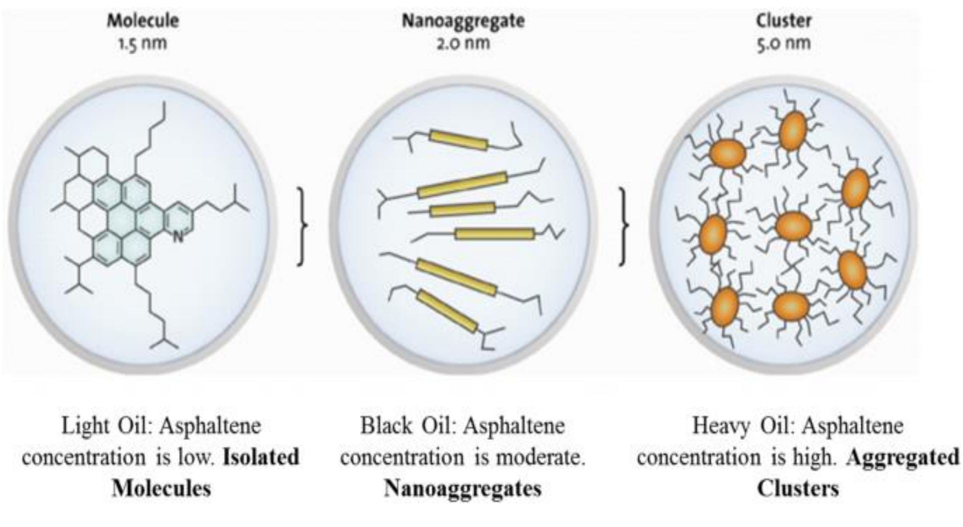

Figure 3
Yen-Mullins asphaltene model (Mullins, 2011)

Naphthenate deposits in crude are solid scales formed by the reaction between naphthenic acid and metal ions basically alkali metals such as calcium and sodium ions in the produced water of the crude samples (Dyer et al., 2003). Naphthenic acid refers to the generic name used for all the organic acids in crude oil, they are indicated by the total acid number (TAN) of the crude (Laredo et al., 2004). An increase in the pH of the produced water from the crude results in the release of CO2 which enables the acids in the crude to combine with the metal ion to produce naphthenate salts or deposits, for instance, calcium naphthenates (CaN) are formed when calcium in the produced water of the crude reacts with naphthenic acid in crude under appropriate pH conditions (Arla et al., 2007; Nordgard et al., 2010). Naphthenates have been known to cause massive challenges in oil field operations worldwide, they can precipitate and form organic deposits which block process and expedition lines resulting in flow assurance difficulties (Dyer et al., 2003). Calcium naphthenates (CaN) can form tight emulsions that can lead to the plugging of oil/water surface separation installations. CaN deposits contain tetraprotic acids (TPA) that is acid with four acidic groups with molecular weight up to 1230 g /mo l (Laredo et al., 2004)? Initially it was assumed that the presence of TPA can be used to indicate the formation or presence of CaN scales however recent analyses have shown that certain crude oils with confirmed presence of TPA were from reservoirs without CaN issues, in other words all CaN scales contain TPA whereas the presence of TPA on its own do not confirm the prevalence of CaN scales (Nordgard et al., 2010).

The aim of this study therefore is to determine the asphaltene, naphthenic acid and naphthenate components (especially calcium and sodium naphthenates) of some crude oil samples obtained from the Niger Delta area of Nigeria. Calcium and sodium naphthenates are of interest because they form organic deposits in production facilities that results in flow assurance difficulties unlike the naphthenates of other metal ions like magnesium and iron, however in the case of naphthenates in crude oil it is important to note that determining the naphthenic acid in the crude is very critical in ascertaining the possibility of metal-naphthenate deposit formation (Laredo et al., 2004). Further studies will be on treatments required to avert or possibly reduce the formation of crude oil solid deposits such as asphaltenes and naphthenates. A typical structure of calcium naphthenate is shown in Figure 4

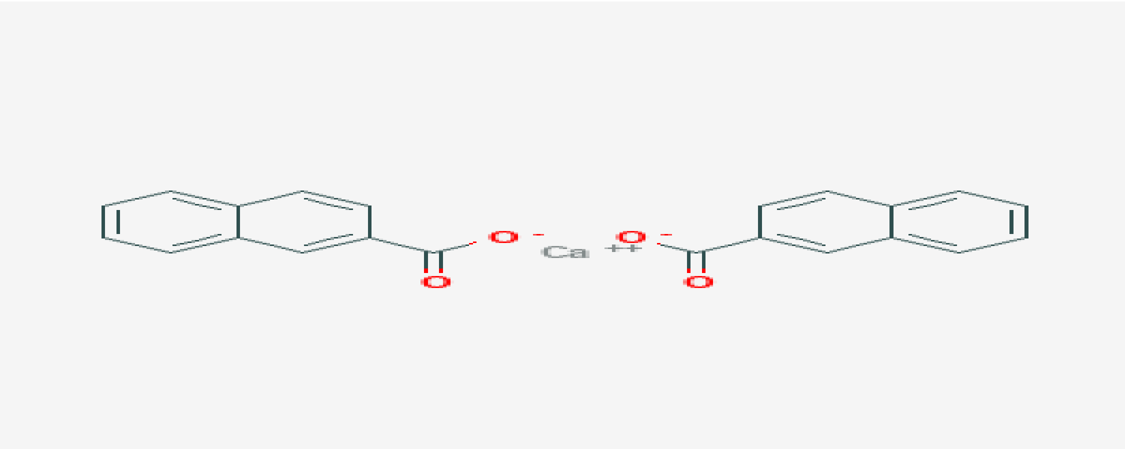

Figure 4
Chemical structure of Calcium naphthenate

2. Materials and methods

2.1. Description of study area and sample collection

The Niger Delta basin is located in the southern part of Nigeria, it is surrounded by the Atlantic Ocean and has a land area of about 141,639 Km2 and sedimentary sequence of 39,600 ft thickness. It lies between a longitude of 50E - 80E and a latitude of 30N - 60N, it is shortened in the west by the Dahomey basin, surrounded in the northwest by the Benin flank, enclosed by the Abakaliki anticlinorium in the northeast. The basin stretches in an east-west direction from southwest Cameroun to Okitipupa ridge and enclosed by older mega tectonic elements such as the Calabar flank. The Niger Delta basin is the most important sedimentary basin in Nigeria in terms of thickness and size of sediments, its petroleum reserve provides the largest foreign exchange earnings in the country and it is currently the leading oil province in Africa (Reijers, 2011). The study area is situated in the western part of the basin, close to the Fercados terminal from an oil producing field labelled FTX as shown in Figure 5. Unpressurised crude oil samples were obtained from ten different oil wells within the field and labelled FT01, FT02, FT03, FT04, FT05, FT06, FT07, FT08, FT09 and FT10 based on the oil wells. The crude samples were obtained with dried 1-Litre glass bottle free from debris and acid components. Crude oil samples under pressure and high temperature could affect the solid deposit concentration of the sample.

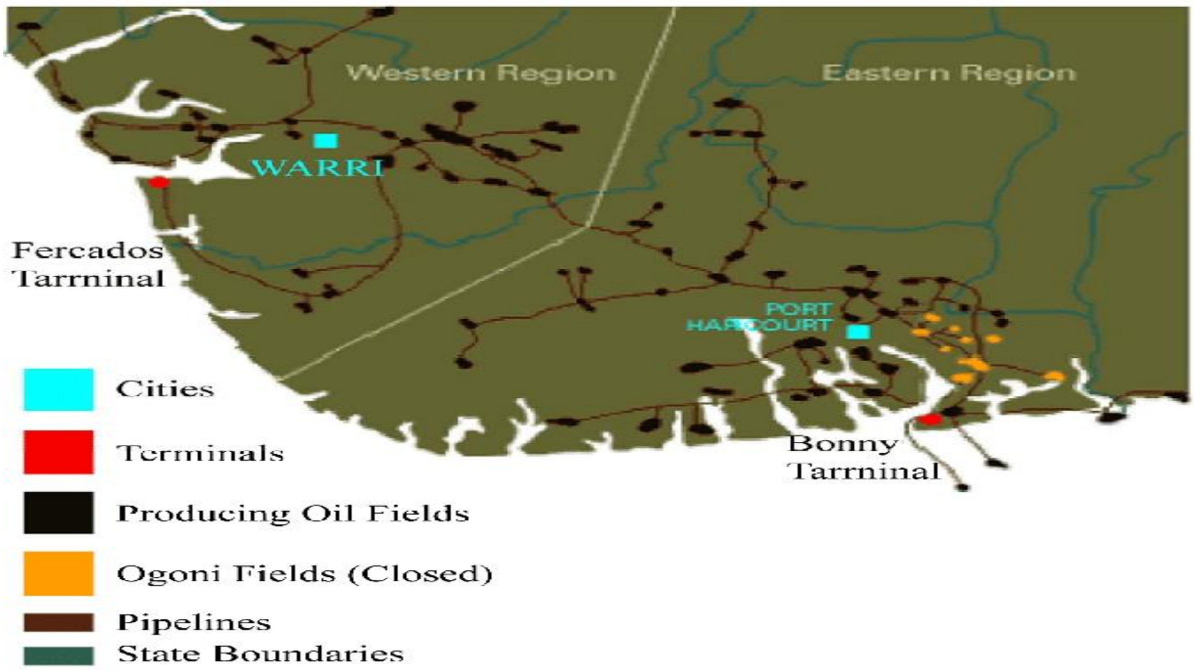

Figure 5

Niger Delta Map showing Producing Oil Fields

2.2. Determination of Asphaltenes (Heptane Insoluble) in Crude oil samples

Aasphaltene (Heptane insoluble) in the crude oil sample was determined by gravimetric analyses. A 100 mL portion of the crude oil sample was mixed with heptane and the mixture heated under reflux. The precipitated asphaltenes, waxy substances and inorganic material are collected on a filter paper, the waxy substances are removed by washing with hot heptane in an extractor while the inorganic material is separated by dissolution in hot toluene, thereby recovering the insoluble asphaltene deposits in the extraction solvent. The extraction solvent is evaporated by heating and the resultant asphaltene is weighed by gravimetry (ASTM D6560)

2.3. Determination of the total acid number (TAN) in crude oil samples

Total acid number (TAN) in the crude oil sample was determined by Potentiometric titration. A blank test was carried out by adding 125 mL of toluene, pure water and 2-propanol (titration solvent) in a volumetric ratio of 100: 1: 95 into a 200 mL beaker, nitrogen gas was blown onto the surface with a flow rate of 200 L/min to eliminate the influence of CO2 in air, titration was carried out with 0.1 mol/L potassium hydroxide 2-propanol solution to measure blank level. Actual measurement was carried out by weighing 20 g of the crude sample (approximately 25 mL) into a 200 mL beaker, 125 mL of the titration solvent was added, nitrogen gas was blown to the surface of the solution at a flow rate of 200 L/min and then titrate with 0.1 mol/L potassium hydroxide 2-propanol (reagent) to measure the total acid number (ASTM D664).

TAN can be calculated using equation 1 as shown below:

$$Total\ acid\ number\ \left(\frac{mgKOH}{g}\right) = (EP1 - BL1) \times \frac{TF \times C1 \times K1}{S} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (1)$$

Where:	EP1	=	Titer for blank (mL)
	BL1	=	End point of blank (mL)
	TF	=	Titration factor of reagent (mL)
	C1	=	Concentration conversion coefficient
	K1	=	Unit conversion coefficient
	S	=	Weight of sample (g)

2.4. Determination of metal ions in produced water from crude oil samples

The metal ions (Ca^{2+} and Na^{+}) in the produced water obtained from the crude samples were determined by atomic absorption spectrometry. Standard solutions containing known concentrations of Ca^{2+} and Na^{+} were obtained from their respectively stock solutions through a dilution process using deionized water for calibration. The concentrations of Ca^{2+} and Na^{+} in the produced water obtained from the crude oil samples were determined using a 700 model Perkin Elmer Atomic Absorption Spectrophotometer (Hill and Fisher, 2017).

2.5. PH determination of produced water from crude oil samples

The pH meter and associated electrodes were calibrated using two reference buffer solutions within the range of the pH anticipated. The sample measurement was carried out under strict controlled conditions and prescribed techniques, minimizing interferences as much as possible. The already calibrated electrodes were immersed into the sample. The pH and temperature are displayed as soon as the electrode output stabilizes. (ASTM D1293, 2015).

2.6. Determination of the specific gravity of crude oil samples

The specific gravity of the crude sample was determined by hydrometer method. A 400 ml graduated cylinder was filled with the sample to be analyzed, a hydrometer with calibration 0.75 was submerged into it, and readings were taken as the hydrometer floats on the sample. A thermometer was inserted into the sample in the graduated cylinder for 10 s and temperature recorded. Specific gravity values corresponding to the temperature in ^{0}C were read as values for the corrected specific gravity (ASTM D1298, 2017)

3. Results

Table 1

Asphaltene, TAN, metal components / physiochemical parameters of crude oil samples

Sample	Asphaltene (%w)	TAN (mgKOH/g)	Specific Gravity @ 15 ^{0}C	^{0}API Gravity	pH	Ca^{2+}(mg/L)	Na^{+}(mg/L)
FT01	6.5000	1.2100	0.8524	34.5000	5.1000	94.5000	105.1000
FT02	3.0000	0.6200	0.8314	38.7000	8.7000	85.5000	78.5000
FT03	2.5000	0.4700	0.8299	39.0000	9.2000	80.5000	99.5000
FT04	8.0000	1.4600	0.8540	34.2000	8.6000	46.6000	65.5000
FT05	2.7000	0.5800	0.8319	38.6000	9.1100	66.6000	37.8000
FT06	3.0000	0.6000	0.8324	38.5000	8.5000	55.5000	49.9000
FT07	4.0000	0.8000	0.8378	37.4000	8.0000	72.2000	66.4000
FT08	5.5000	1.1100	0.8428	36.4000	7.8000	32.5000	79.4000
FT09	2.0000	0.3000	0.8398	40.0000	6.5000	64.2000	27.7000
FT10	4.5000	1.0100	0.8408	36.8000	7.9000	72.2000	66.8000

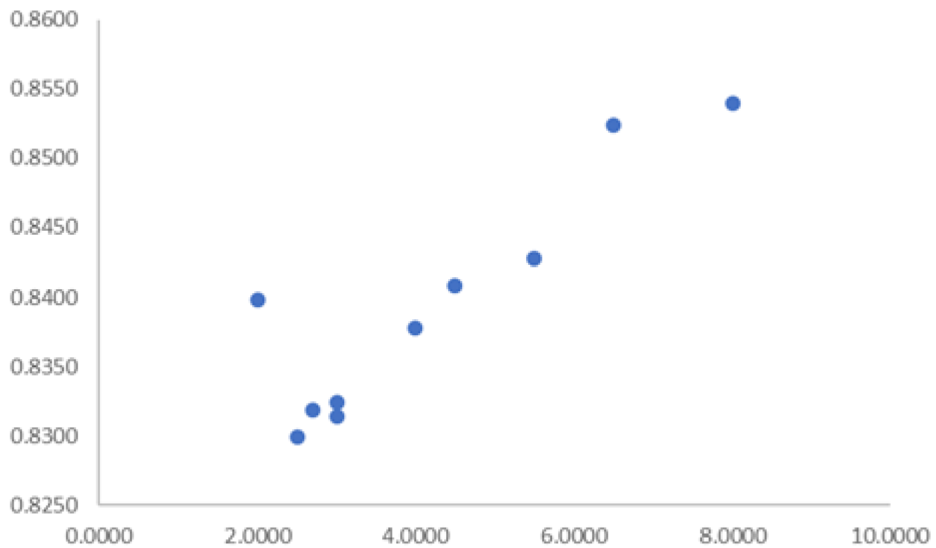

Figure 6

Plot of specific gravity versus asphaltene (%w) of crude oil sample

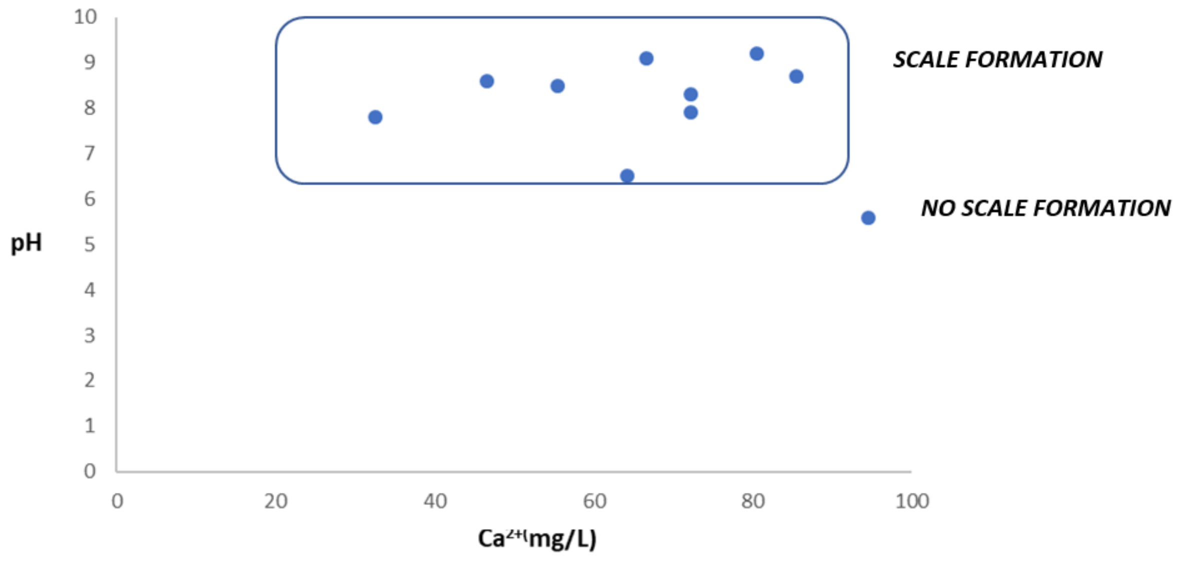

Figure 7

Plot of pH versus Ca^{2+}(mg/L) in crude oil samples

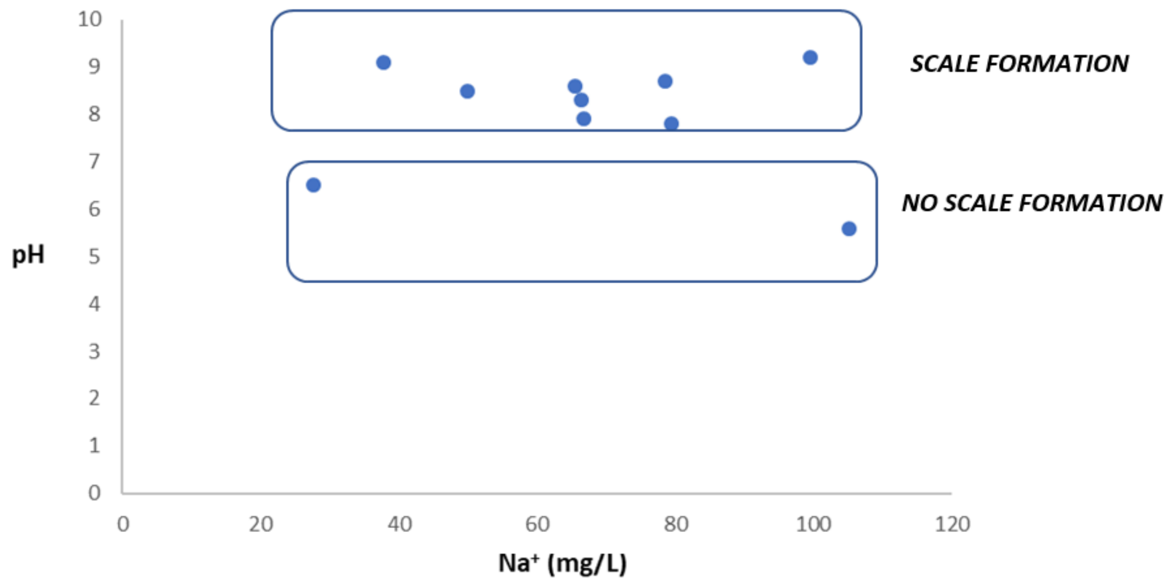

Figure 8

Plot of pH versus Na^{+}(mg/L) in crude oil samples

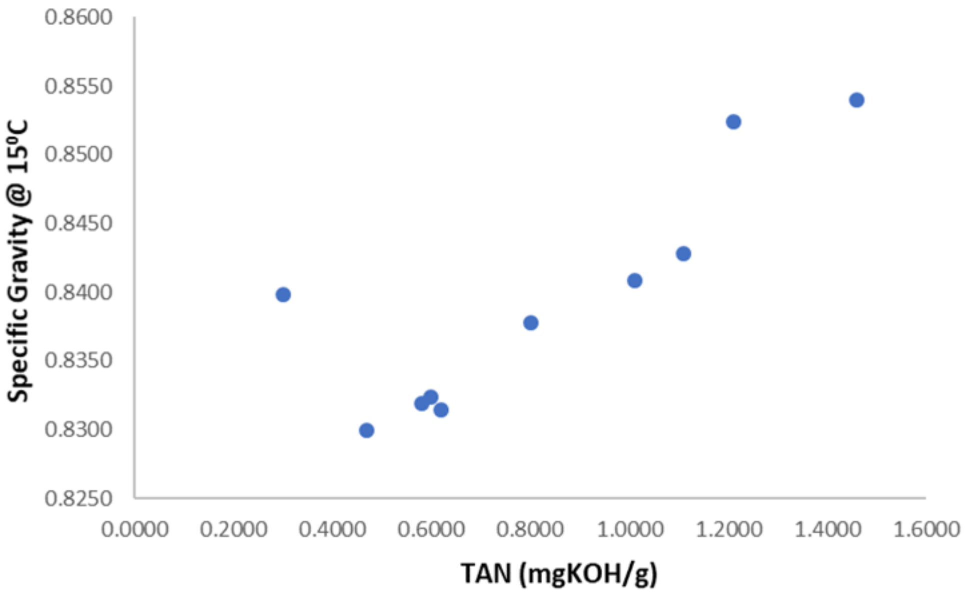

Figure 9

Plot of Specific gravity versus TAN (mgKOH/g) of crude oil samples

Flow assurance difficulties happen to be one of the major challenges faced in crude oil exploration and they are basically caused by solid deposits in the crude. Asphaltene is one of the solid components of crude oil known to cause a lot of problems during crude oil exploration and transportation from the reservoir. Asphaltenes are highly problematic because of their ability to form dense flocculation and deposits in reservoir, wellbores and transportation pipelines (Alrashidi et al., 2018). Figure 6 shows a plot of specific gravity versus the asphaltene components of crude samples, the asphaltene in light oils with low specific gravity and high API gravity are usually in the form of small polyaromatic hydrocarbon molecules with an average diameter of 1.5 nm while in black oils with high specific gravity and low API gravity the asphaltene concentration is usually higher and are present in the form of nanoaggregates with an average diameter of 2 nm, the asphaltene concentration in heavy oils with extremely low API gravity is relatively high and are present in the form of clusters hence the asphaltene concentration in crude oil is inversely proportional to the API gravity and directly proportional to the specific gravity as shown in Table 1. Well FT01 has the least API gravity and with the highest asphaltene concentration while well FT09 has the highest API gravity with the lowest asphaltene concentration, this is affirmed by the Yen-Mullins model of asphaltene structure as shown in figure 3. Based on this model, the oil becomes heavier as the asphaltene concentration in the oil increases and this ultimately leads to the decrease in the API gravity hence asphaltenes have an overall negative impact on the crude (Mullins 2011).

The asphaltene deposits in crude oil goes through several phases in the crude depending on its stability and its consistency in solution under the operational and thermodynamic conditions at which it is being produced (Soroush et al., 2014). The asphaltene components of the crude remains stable as long as the equilibrium between it and the liquid components of the crude is intact, however the asphaltene begins to precipitate once a disturbance in the equilibrium condition occurs (Kuznicki et al., 2008). An increase in asphaltene precipitation results in larger asphaltene flocculation with higher density than the precipitated particles which ultimately deposits in the reservoir pores, wellbores or pipelines (Soroush et al., 2014). Asphaltene deposition can cause several problems in oil exploration such as adsorption on the rock surface, pore plugging, wettability and crude oil parameter alteration as well as reduction in oil recovery (Alrashidi et al., 2018). It is however worthy to note that if the asphaltene particles are noticed early at the precipitation stage an adequate remedial technique can be applied to breakdown the flocculation back to smaller precipitated particles, if this occurs the smaller precipitated particles can be homogenized back in the crude with the use of a stabilizing chemical reagent (Dyer et al., 2003). The primary precaution that must be applied to prevent asphaltene deposition is the maintenance of the equilibrium between the asphaltene and the liquid content of the crude however operational factors and reservoir factors can lead to the upset in this equilibrium (Kuznicki et al., 2008). Operational factors include solvent injection, solvent concentration and electro kinetic effects while reservoir factors include pressure, temperature, solution gas, oil viscosity and oil concentration (Soroush et al., 2014).

Apart from asphaltene, another solid deposit of concern in crude oil which causes flow assurance difficulties are naphthenates. An increase in the production of acidic crudes with high concentration of naphthenic acids have been a cause for concern in the oil and gas industry in recent past (Laredo et al., 2004). Acidic crude poses major concerns as regards flow assurance in crude processing plants as well as process control, these concerns ranges from naphthenic acid corrosion (NAC) and formation of naphthenates which can either precipitate and form organic deposits or form interfacial active salts prone to stabilized emulsions (Nordgard et al., 2010). The organic deposits so formed have the ability to block process flow lines and vessels thereby resulting in flow assurances challenges (Opeyemi et al., 2021). The naphthenic acid concentration in crude are measured by their total acid number (TAN) as seen in Table 1. The phase behavior of the naphthenic acid in crude is determined by the composition and pH of produced water of the crude (Arla et al., 2007). The naphthenic acid as well as other tetraprotic acid (TPA) in crude may react with the cations present in the produced water of the crude at a pH > 6 to form naphthenate scale deposits in other words, the produced water pH and availability of cations play an important role in the formation of naphthenate scales. Calcium naphthenate scale formation is more favored at brine pH > 6 while sodium scale formation is favored at a pH of approximately 8.5 (Opeyemi et al., 2021). Increase in produced water pH during crude oil production are usually caused during depressurization and release of CO2 (Arla et al., 2007). Results obtained from Table 1 show that well FT01 has the highest concentration of Ca2+ and Na+ as well as the second highest naphthenic acid concentration as indicated by the TAN however the formation of calcium and sodium naphthenate scales might be impeded due to the produced water pH which is < 6. It has been reported by several experiments that at low produced water pH, precipitation do not occur as metal naphthenates do not precipitate at produced water pH < 6 (Laredo et al., 2004). A plot of pH versus Ca2+ concentration is shown in Figure 7, from the plot it can be deduced that the crude oil from well FT01 has no tendency of forming calcium naphthenate scales. On the other hand, the other wells have a high propensity of calcium and sodium naphthenate formation with wells FT02, FT03, FT04, FT05 and FT06 favoring the formation of more sodium naphthenate scales and FT07, FT08, FT09, FT10 favoring the formation of more calcium naphthenates due to the slight variations in the pH of the produced water of the crude. A plot of pH versus Na+ concentration is shown in figure 8, from the plot, it can be deduced that the crude oil from FT01 and FT09 have no tendency of sodium naphthenate scale formation (Nordgard et al., 2010). Results have shown that most crude oils with high tendency of calcium naphthenate scale formation always have higher TAN of (0.40 – 2.50 mgKOH/g) while crude oils with high tendency of sodium naphthenate scale formation always show low TAN of (0.20 – 0.60 mgKOH/g) however it is worthy to note that most calcium naphthenate forming crudes may have low TAN due to the pH of the produced water just as in the case of sample FT09. The crude oil from well FT04 though with a high TAN may favor more formation of sodium naphthenate scales due to the pH of the produced water (Laredo et al., 2004). The relationship between the specific gravity and TAN of crude oil can serve as a guide to ascertain the effect of TAN on the ability of crude to form calcium and sodium naphthenate deposits respectively. A plot of specific gravity and the TAN of crude oil samples is shown in figure 9, results obtained show that the higher the TAN of the crude, the higher the specific gravity and subsequently the higher the probability for the crude to form both calcium and sodium naphthenate deposit scales (Opeyemi et al., 2021).

4. Conclusion

The blockage of crude oil expedition lines and well bores by solid deposits in crude poses a lot of flow assurance challenges during crude oil production. Asphaltene is a complex high molecular weight solubility class deposit in crude, it is directly proportional to the specific gravity and inversely proportional to the API gravity, its precipitation is dependent on the disturbance of the equilibrium between it and the liquid phase of the crude. Operational and reservoir factors are responsible for this upset as such the behavior of asphaltenes in crude depends on the conditions available in the reservoir. Metal naphthenates such as calcium and sodium naphthenates are formed by the reaction between naphthenic acids and other tetraprotic acid (TPA) in crude with metal ions in the produced water of the crude at appropriate pH and other compositional conditions. This study unveils the asphaltene content and the factors that determines the formation of calcium and sodium naphthenates in crude oils and this gave rise to the following findings:

i. The formation of calcium naphthenate scale deposits are more when the pH of the brine is slightly above 6 while sodium naphthenate scales are formed more at an approximate pH of 8.5.

ii. All the crude oil samples except one could form naphthenate scales based on their respective TAN, pH of produced water and metal ion concentrations. The higher the TAN of the crude, the higher the specific gravity and the lower the API gravity which in turn results in a higher possibility of metal naphthenate scale formation.

iii. An in-depth knowledge of the solid deposits (asphaltene and naphthenate scale deposits) in crude oil is vital in determining the appropriate treatment program suitable for the crude by way of choice of treatment chemicals, chemical composition of chemicals as well as frequency of injection.

One of the important factors that can hamper a successful crude oil production is the inability to be assured of a free flow of the crude to desired destinations. Solid deposits in crude such as asphaltenes and metal-naphthenates are major culprits as far as the free flow of crude is concern.

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