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EVALUATION OF DISPERSED WATER FROM CRUDE OIL BLEND AND ITS EFFECTS ON CRUDE OIL PROPERTIES AND PRODUCTION EQUIPMENT

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ABSTRACT

Dispersed water from crude oil obtained from ten different producing wells in the Niger Delta area of Nigeria were analyzed based on American Standard for Testing and Materials to determine the effects of the physicochemical properties on crude characteristics and the production equipment. Results (in bracket) were: pH (7.51-8.60), salinity (11174.00 - 21469.00 mg/l), conductivity (12698.00 - 24396.00 µS/cm), sulphate (3.00 - 23.00 mg/l), Total hardness (20.00 - 46.00 mg/l), water cut (12.10-58.83 %). The pH, salinity and conductivity of the dispersed water from all the crude samples were within specification as recommended by American Petroleum Institute. The sulphate concentration of the dispersed water from crude samples 1, 9 and 10 were above specification. Also, the total hardness of the dispersed water from crude samples 1, 3 and 6 were above the maximum allowable limit of 40.00mg/l set by American Petroleum Institute. High sulphate content in Crude oil increases the hydrogen sulphide concentration due to activities of sulphate reducing bacteria which is harmful to both the environment and production equipment. High concentration of magnesium and calcium ions in crude oil causes scale formation leading to coat perforations damages to casing, production tubulars, valves, pumps, and down hole completion equipment.

Keywords: Brine, demulsification, dissolved water; emulsion, hydrophobic, oil recovery.

INTRODUCTION

Water in crude oil has been a major challenge in the oil and gas industry, not just in upstream oil production but also in downstream refining, distribution and transmission [1]. Most petroleum industries produce an average of three barrels of water for each barrel of oil from depleting reservoirs and more than 40 billion United States dollars is spent dealing with unwanted water. Saline water could either be dissolved water or dispersed water and it derives its name because of its salt content [2]. At higher temperatures, water shows a remarkable solubility in crude oil. About 0.4% water might be dissolved at temperatures of approximately 149°C [3]. Dissolved water in crude oil which is also known as the entrapped water is the amount of water in the crude oil after separation, it is also called residual water whereas dispersed water is the water that can be separated from the crude and is often obtained alongside the sediments in the crude through demulsification, it is also called free water or water-in oil emulsion [4]. Demulsification is the separation of a crude oil emulsion into oil and water phases. When the dispersed water is determined with the sediments and emulsion, it is calculated as 'basic sediment and water' (BS&W), whereas when determined alone, it is calculated as the water cut of the crude [5]. Though dispersed water, produced water and dissolved water are obtained from the reservoir during crude oil production, produced water is a byproduct of the production of oil and gas from underground reservoirs and can be said to be part of the source of dispersed and dissolved water [1]. Dissolved and dispersed water are contaminants in crude oil hence undesirable. Their content and the properties vary from one field to another. While it is possible to separate dispersed water from the crude, it is impossible to separate the dissolved water. However, the dispersed water is a reflection of the properties of the dissolved water though at a higher concentration since both (dissolved and dispersed water) are from the crude oil [6].

The aim of this study is to determine the physicochemical parameters of dispersed water from a crude oil blend obtained from different wells, evaluate their effects on crude characteristics as well as the process equipment used in crude production.

MATERIALS AND METHODS

Sample Collection, Preparation and Analyses

Crude oil samples were obtained from ten different producing wells in the Niger Delta with a record of high BS&W (> 2%) with sampling bottles that were rinsed properly with xylene, air dried and rinsed with the sample. Triplicate samples were obtained from each well and an average of the result was reported. The dispersed water samples obtained from the respective crude were labeled samples 1, 2, 3, 4, 5, 6, 7, 8, 9 and 10 corresponding to the numbering of the respective wells.

Determination of Water Cut of the Crude

The water cut of each of the crude sample was determined using Rotanta 460R Petroleum centrifuge. The dispersed water was obtained with the use of a clean pipette immersed into the crude sample contained in a centrifuge bottle sucking up the water from the base. Analytical tests such as pH, conductivity, salinity, sulphate concentration, calcium and magnesium ions (total hardness) of the dispersed water samples were determined based on American Standard for Testing and Materials (ASTM).

Determination of Sulphate ion in Dispersed Water

10ml of standard solution and 10ml of distilled water were added to a 250 ml Erlenmeyer flask in addition to 5.0ml of the conditioning reagent and stirred gently. 0.1 to 0.2g of 20 to 30 mesh $BaCl_2$ was carefully added to the flask. The prepared content was poured into the nephelometric cell, and let to stand for five minutes. Similar preparation was carried out on the dispersed water sample. An absorbance versus concentration curve was created with the original concentration of the standard to obtain the sulphate concentration of the sample [7].

2.4 Determination of Calcium and Magnesium ion in Dispersed Water (Total hardness)

Ethelenediaminetetraacetic acid (EDTA) a chelating agent was added to the dispersed water sample after the pH of the solution was adjusted to 10 with ammonium hydroxide for the determination of magnesium ions and 12 with sodium hydroxide for the determination of calcium ions. The end point was observed through complexmetric titration with a suitable indicator [8].

RESULTS AND DISCUSSION

Table 1. pH and Salinity of Dispersed Water samples

Dispersed Water sample	pH				Salinity (mg/l)			
	1st	2nd	3rd	Average	1st	2nd	3rd	Average
1	8.52	8.56	8.46	8.51	19012.00	19008.00	19011.00	19010.33
2	8.21	8.20	8.28	8.23	16146.00	16244.00	16152.00	16180.67
3	8.20	8.23	8.23	8.22	19773.00	19701.00	19791.00	19755.00
4	7.33	7.36	7.40	7.36	14684.00	14691.00	14625.00	14666.67
5	7.90	7.89	7.90	7.90	21002.00	21104.00	21009.00	21038.33
6	8.60	8.60	8.60	8.60	21469.00	21555.00	21447.00	21490.33
7	7.11	7.20	7.20	7.17	12051.00	12300.00	12028.00	12126.33

8	8.25	8.23	8.25	8.25	16556.00	16552.00	16549.00	16552.33
9	8.02	8.03	8.00	8.02	20358.00	20359.00	20411.00	20376.00
10	7.51	7.53	7.52	7.52	11174.00	11165.00	11182.00	11173.67
API SPEC.			**6.5-9.0**			**≤35000**		

Table 2. Sulphate Concentration and Conductivity of Dispersed Water samples

Dispersed Water sample	Sulphate (mg/l)				Conductivity (µs/cm)			
	1st	2nd	3rd	Average	1st	2nd	3rd	Average
1	23.00	24.00	23.00	23.33	21604.00	21552.00	21478.00	21544.67
2	12.00	12.00	11.00	11.67	18348.00	18222.00	13154.00	16574.67
3	8.00	8.00	9.00	8.33	22470.00	22349.00	22466.00	22428.33
4	6.00	7.00	7.00	6.67	16686.00	16522.00	16678.00	16628.67
5	14.00	13.00	15.00	14.00	23865.00	23598.00	23722.00	23728.33
6	3.00	3.00	4.00	3.33	24396.00	24411.00	24399.00	24402.00
7	6.00	6.00	6.00	6.00	13694.00	13692.00	13688.00	13691.33
8	10.00	10.00	10.00	10.00	18814.00	18825.00	18814.00	18817.67
9	20.00	21.00	20.00	20.33	23135.00	23211.00	23197.00	23181.00
10	21.00	21.00	20.00	20.67	12698.00	12655.00	12702.00	12685.00
API SPEC			**≤16**				**≤35000**	

Table 3. Total hardness and Water cut of Dispersed Water samples

Dispersed Water sample	Total hardness (mg/l)				Water cut (%)			
	1st	2nd	3rd	Average	1st	2nd	3rd	Average
1	46.00	46.00	45.00	45.67	12.10	12.20	12.05	12.12
2	38.00	37.00	36.00	37.00	15.15	15.08	15.12	15.12
3	40.00	40.00	40.00	40.00	14.38	14.15	14.22	14.25
4	22.00	22.00	21.00	21.67	22.01	22.05	22.00	22.02
5	42.00	41.00	43.00	42.00	18.65	18.72	18.66	18.68
6	55.00	55.00	56.00	55.33	33.58	33.71	33.55	33.61
7	24.00	23.00	24.00	23.67	45.25	45.09	45.18	45.17
8	20.00	20.00	20.00	20.00	20.01	20.11	20.05	20.06
9	28.00	26.00	28.00	27.33	55.32	55.01	55.33	55.22
10	24.00	22.00	24.00	23.33	58.83	58.81	58.74	58.79
API SPEC		**10**	**to 40**					

The emulsion stability of the crude is highly influenced by the pH of dispersed water and this affects the stability of the interfacial films. The strength of the interfacial films decreases as the pH increases. They are converted to mobile films within a high pH. However, the reverse is the case for films formed by resins which are strongest within an alkaline range and become progressively weak within an acidic range [9]. The type of emulsion formed is also influenced by the pH. Water-in-oil emulsions are produced within an acidic range or when the pH is low whereas oil-in-water emulsions are produced within an alkaline range or when the pH is high [5]. If the water in oil is acidic, the volume of dispersed water calculated as the water cut (%) will be reduced due to the increased interfacial tension between the water and oil and this reduces the oil recovery. On the other hand, if the water-in-oil is alkaline, the volume of dispersed water calculated as water cut (%) increases and this enhances oil recovery [3]. Optimal pH for water separation varies for distilled water and brine solution with the former as 10 and the latter between 6 and 7 due to ionization effect that is interaction between the asphaltenes and ions present in the brine solution [10]. The pH of the dispersed water should be between 6.5 and 9.0; however acid injection for pH control is carried out if higher values are expected. Stable emulsions are enhanced within the acidic range, whereas pH values < 6.5 may lead to corrosion of metallic parts [11]. Table 1 shows that the pH of the dispersed water samples of the crude oil obtained from the ten (10) wells were within American Petroleum Institute specification (6.5 – 9.0) [15].

The water cut of the crude is the amount of water in the crude measured from the oil water interface to the water base after separation using a suitable demulsifier. It is often calculated in percentage [12]. It has been observed that an increased water cut gives rise to growth of thixotropic properties and dispersed system structuring. Thixotrophic properties refer to the ability of a fluid to be thick or viscous when stirred or shaken and returning to a semi solid state upon standing [3]. Water and sediment have the tendency of fouling heaters, steels and exchangers and can result in corrosion as well as undesirable product quality [9]. The sludge that accumulates in storage tanks are made up of water and sediment and this must be disposed of periodically in an environmentally acceptable manner. Water in storage tanks can promote microbial activities which can lead to the production of corrosive acids and hydrogen sulfides even if the system is anaerobic. However, this problem is circumvented by rotating crude oils and stocks on a regular basis. Nonetheless anaerobic degradation of crude oil stocks has been known to occur [1]. Table 3 shows the water cut of the crude from different wells. Results show that the dispersed water of the crude from well 10 (sample 10) has the highest water cut while the dispersed water of the crude from well 1 (Sample 1) has the least water cut.

Crude oil salinity consists of salt dissolved in small droplets of water which are dispersed in the crude. Sometimes the oil produced contains crystalline salt arising from pressure and temperature changes as well as stripping of water vapor as the fluid flows up the wellbore and through the production equipment [11]. The salinity of the brine used determines the residual oil saturation obtained at the end of a water injection process. Water flooding is the use of water injection to increase the production from oil reservoirs [13]. Brine refers to salt water used in completion operations especially when penetrating a pay zone during drilling operations. Brines are preferred to fresh water because they have higher densities and lack solid particles that might damage producible formations [14]. The oil/brine ratio (OBR) is used to compare solids content and salinities of oil mud [11]. Crude oils with very low or high pH with large acid or base numbers with a high surface charge density at the oil/water interface, interactions between polar fractions are expected to dominate and the trend seen can be explained in terms of the instability of brine films at high salinity leading to reduced oil recovery [9]. The function of crude oil composition with respect to the salinity dependence on wettability and oil recovery is a more difficult problem to resolve [11]. Connate water refers to water trapped in the pores of a rock during rock formation, it can be dense and saline compared to seawater and one of the primary source of water in crude [2]. The salinity dependence on oil recovery during water flooding is not limited to crudes with low pH. Imbibition experiments have shown strong salinity dependence on other classes of crude. Imbibition is the process of absorbing a wetting phase into rock with high permeability. It is important in a water drive reservoir because it can promote or prevent water movement thereby affecting areal sweep [13]. The salinity of the water entrapped in rocks has been discovered to be the primary factor controlling oil recovery. It has been already well established that adjusting the salinity of displacing fluid critically affects the oil recovery efficiency during secondary and tertiary oil recovery processes. The salinity of the displacing fluid is inversely proportional to the oil recovery. The use of displacing fluids with low salinity guaranties a higher oil recovery [2]. In addition, emulsion stability decreases with increasing water phase salinity. Most dispersed water contains salts that can cause corrosion problems in production and refining. [4]. API specifies salinity ≤ 35000 mg/l for any crude with water content > 2.0%. Table 1 shows that the salinity of all the samples analyzed were within API specification [15].

The salt content of crude oil can also be measured with respect to the conductivity of the crude. For many years, the salinity of crude oil is routinely determined by comparing the conductivity of crude oil in water to that of a series of standard salt solutions in water [16]. Salts in crude oil may have a harmful effect in several ways, even in small concentrations. Salts in crude accumulate in steels, heaters and exchangers leading to fouling that requires expensive clean up [9]. The injection of an alkaline compound such as ammonia is necessary in this case owing to the emission of the highly corrosive acid capable of corrosion [3]. Contamination of both overhead and residual products as well as deactivation of catalyst can also result from the activities of salts and evolved acids [2].

The concentration of barium and calcium ions in dispersed water is inversely proportional to the sulphate concentration in the water. The lower the sulphate concentration, the higher the tendency of barium and calcium ion formation which in turn reduces the probability of barium and calcium scales formation [17]. In addition, the higher the sulphate concentration in crude oil, the higher the hydrogen sulphide (H_2S) concentration released from the crude due to activities of sulphate reducing bacteria (SRB). H_2S which is extremely harmful if inhaled could easily escape from contaminated liquids. Soured oil or natural gas has a high percentage of hydrogen sulfide (>0.5%). Natural gas with a concentration of up to 28% hydrogen sulphide gas could be an air pollutant near petroleum refineries and in oil and gas extraction areas [18]. SRB are harmful bacteria during oil and gas production. They are capable of causing serious problems in water systems of oil fields such as produced water systems, corrosion of iron even without oxygen and reduction of the injectivity of water injection wells by amorphous ferrous sulfide precipitation [19]. SRB could drastically reduce oil viscosity, restore the reduced pressure of reservoir, and transform heavy oil to light oil through the formation of naturally produced acids such as H_2S and breaking down of hydrocarbons (Aliphatic and Aromatic) [4, 20]. API specifies a maximum of 16 mg/l sulphate concentration for the dispersed water in crude oil. Table 2 shows that samples 1, 9 and 10 were above specification therefore liable to release high concentration of hydrogen sulphide [15].

Calcium and magnesium ions are responsible for total hardness of water. Calcium and magnesium ions found in dispersed water in the presence of sulphate ions are responsible for the scale forming abilities of crude oil. Wells producing water with high concentration of calcium and magnesium ions are likely to develop deposits of inorganic scales [14]. Scales are capable of coating holes punched in the casing or liner of an oil well thereby reducing communication path between the well bore and the reservoir. They could also lead to the coating of other production equipment such as production tubulars, valves, pumps and drilling equipment such as safety equipment and gas lift mandrels. If no intervention is applied such as antiscale treatment, scaling could drastically reduce production which could result in subsequent abandonment of the well [21]. API specifies an average of 10 to 40mg/l combined concentration of magnesium and calcium (total hardness) for dispersed water in crude oil. Table 3 shows that samples 1, 3 and 6 are not within specification as such are liable to form variety of scales if anti scale treatment is not carried out [15].

CONCLUSION

Dissolved and dispersed water are contaminants in crude oil hence undesirable in the crude. The properties of the dispersed water give an incline on the effects of the dissolved water both on the crude characteristics and production equipment. Crude oil from three out of ten production wells has sulphate concentrations and total hardness above API Specification. Oil wells producing crude oil with high sulphate concentration have the tendency of producing soured crude through the reduction of sulphate ions to hydrogen sulphide by the activities of sulphate reducing bacteria. Crude oil with high hydrogen sulphide concentration is harmful to both human and the environment as well as oil field water systems. Crude oil with high magnesium and calcium concentration (total hardness) has the ability of forming scales which can limit production thereby resulting in the eventual abandonment of the well.

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