

Analysis of Formation Water Compositions and Its Effect on Crude Oil from Off-Shore Location of Niger-Delta, Nigeria

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Abstract: *This experimental research work analysed the compositions of formation water and its effect on crude oil from an offshore location off the shore of central Niger-Delta Area of Nigeria. Some specific chemical and microbiological analyses were determined at laboratory temperature (77°F) and formation temperature (182°F). Analysis of the mixture of formation water and crude oil were carried out at various ratios (90:10 and 50:50) respectively. Test result indicated that the influx of formation water sample into crude oil resulted in an increased in concentration of most of the parameters both at laboratory and formation temperature. It was observed that some physicochemical parameters like (PH, TDS, and Electrical conductivity) showed a much higher concentration values at the formation temperature than laboratory temperature. While the PH values for 90/10 ratio at both laboratory and formation temperature gave 4.90 mg/l and 6.45 mg/l, the values for 50/50 ratio at both laboratory and formation temperature were 5.30 mg/l and 7.94 mg/l respectively. The total dissolved solids (TDS) for 90/10 ratio at both laboratory and formation temperature were 57 mg/l and 70 mg/l respectively. While 50/50 ratio at both laboratory and formation temperature were 73 mg/ and 108 mg/ respectively. The Iron concentration for 90/10 and 50/50 ratio at both laboratory and formation temperature were 0.22, 0.19 mg/ and 0.24, 0.2 mg/l respectively. Therefore in order to produce high quality crude oil with low level of contaminants, the influx of formation water into crude oil should be controlled at both the drilling and production stage*

Keyword: Physicochemical parameters, Formation water, Electrical conductivity, Total dissolved solid, offshore

1. Introduction

Formation water is the water which is found to be present in the oil reservoir with the crude oil initially without any fluid injection and becomes produced water when the reservoir is produced and these fluids are brought to the surface. This formation water can be classified into three generically group each originating from different sources and also differ in composition. The three groups generally identified are: meteoric water, connate water and mixed water [1].

Meteoric water is the water that has its source from rain water, it is the water that has fallen as rain and as filled up the porous and permeable layer, analysis of this water type shows that it contains combined oxygen chiefly carbon-dioxide. These above the ground water table where oxygen react with the sulphide to produce sulphate and carbon-dioxide react to produce carbonate and bi-carbonates. The presence of carbonate, bicarbonate (hydrogen-carbonate), and sulphate in oil field water suggest that at least some of the water had probably come from the surface [3], [5].

Connate water is generally believed to be sea water, in which marine sediment were deposited presumable it originally filled all the pores, it is doubtful, however, whether connate water area actually the original water in place, the current usage is that connate water is that interstitial water existing in reservoir prior to the disturbance of the reservoir by drilling, but actually most reservoir water quite different in chemical composition from sea water, they are undoubtedly circulated and moved in fact have probably been completely replaced since sediments are deposited. Most formation water are brines, characterized by an abundance of chloride especially so called chloride, and they often have concentration of dissolved solid many times greater than mother sea water. This means if the dissolved

mineral content of the ancient sea was approximated the same as that of present sea, that original water has acquired some additional mineral matter since it entered the rock [5].

The chemical analysis of mixed water shows that it is characterised by both a chloride and sulphate carbonate-bicarbonate content. This suggests a multiple origin. Presumably meteoric connate mixed with or partially displaced the connate water of the rock mixed water may occur near the present ground surface or may be found below unconformities [8], [2].

Produced water is therefore not a single commodity. The physical and chemical properties of produced water vary considerably depending on the geographic location of the field, the geological formation with which the produced water has been in contact for thousands of years, and the type of hydrocarbon product being produced. Produced water properties and volume can even vary throughout the lifetime of a reservoir. If water-flooding operations are conducted, these properties and volumes may vary even more dramatically as additional water is injected into the formation.

Knowledge of the constituents of specific produced waters is needed for regulatory compliance and for selecting management/disposal options such as secondary recovery and disposal. Oil and grease are the constituents of produced water that receive the most attention in both onshore and offshore operations, while salt content (expressed as salinity, conductivity, or TDS) is a primary constituent of concern in onshore operations.

In addition, produced water contains many organic and inorganic compounds. These vary greatly from location to location and even over time in the same well. The organic

and inorganic components of produced water discharged from offshore wells can be in a variety of physical states including solution, suspension, emulsion, adsorbed particles, and particulates [4].

Formation water analysis therefore plays a role in dynamic modelling of reservoirs, quantifying reserves and calculating completion cost, including how much will be spent on casing and surface equipment-capital expenditures (capex). Water analysis also helps operators estimate operating expenditures (opex), such as the cost of chemical injection. Quantifying water chemistry aids in the understanding of reservoir connectivity and in characterizing transition zone in carbonates, thereby impacting estimates of reservoir extent. It helps development planner determine whether new discoveries can be tied into existing infrastructure and is crucial for designing water injection projects. The objective of this research work therefore is to analyse the constituents of the formation water, as well as to determine the effect of the formation water on the crude oil from the oil well.

2. Materials and Methods

Sampling: All the collected samples were preserved in accordance with guidelines and International Standards. All other QA/QC procedures relevant to sample collection, custody and analyses were strictly adhered to (APHA 1995; ASTM, 1979).

Physico-chemical analysis: ph/temperature (apha 460), conductivity (apha 145), and tds (apha 208d): These chemical properties were determined electrometrically with a multi-parameter data logger (Hanna model HI991300).

Chloride (APHA 2520A): These were determined titrimetrically. About 25ml of the sample was measured in a beaker and a drop of potassium chromate indicator added. The solution was titrated with AgNO₃ solution until the appearance of brick red colour as the end point. The amount of chlorine (mg/l) was obtained as

$$CL = \frac{(F \times 0.3 \times 1000)}{V}$$

Where F = volume of AgNO₃ titrated and V = volume of sample

Ammonia (APHA 4500C): About 50ml of the sample was measured into distillation flask. 0.4g of magnesium oxide was added and distilled into a beaker containing 10ml of 2% boric acid and combined indicator. This was titrated back with 0.1M HCl and the titre value was recorded.

$$NH_3 \text{ (Mg/l)} = \frac{(F \times 100)}{V}$$

Where F = titre value and V = sample volume used

Phosphate Determination (APHA 425C): About 1 drop of phenolphthalein indicator was added to 100 ml of the sample. 4ml of the molybdate reagent was added and mixed thoroughly. About 0.5ml stannous chloride was added, making sure that all reagents were maintained between 20-30°C. After 10 minutes, the absorbance was measured at 690nm with 10mm cell curvet.

$$PO_4^{3-} \text{ (Mg/l)} = \frac{(F \times 100 \times D)}{V}$$

Where F= reading from curve, D = dilution factor.

Sulphate Determination (APHA 427C): About 20ml

Buffer solution A was added to 100ml of the sample and the contents mixed. While stirring, a spoonful of barium chloride crystals was added and timing was started immediately. After 1min stirring at constant speed, the solution was poured into 10mm cell and measured within 5mins at 425nm.

$$SO_4^{2-} \text{ (mg/l)} = \frac{F \times 100}{V}$$

Where F = reading from curve, D = dilution factor.

Heavy Metals Determination (AAS): Samples were pre-treated with 2ml conc. HNO₃ per litre of sample. The equipment was conditioned by auto-zeroing it with distilled water and with conc. HNO₃. The pre-treated sample was analysed for heavy metals using the appropriate hollow cathode element of each metal of interest at the appropriate wavelength, lamp current, band-pass, and background correction.

PH Value determination

The 25ml was filled with the samples to just sufficient depth to allow immersion of electrode. Mixing was carried out using a gentle shaker and stirred frequently for few minutes, then allow standing for further 15 minutes. The electrode of the meter was immersed into the slurry and waited for needle drift to cease. The pH was recorded for each sample.

Oil and Grease Determination (ASTM D 3921): About 100ml acidified sample (pH 2) was measured into a graduated glass bottle. 4ml of an organic solvent was added to the sample and the bottle vigorously shook for 2mins. The contents of the bottle were emptied into a separating funnel and shook vigorously. The stopper of the funnel was intermittently opened to release pressure build up. The contents of the funnel were allowed to settle. The bottom layer of the solution was transferred into a clean beaker using glass funnel previously stuffed with cotton wool and 1g anhydrous sodium sulphate at the aperture of the glass funnel to absorb water.

MICROBIOLOGICAL QUALITY: Total Heterotrophic

Bacteria (APHA 9215B): About 1ml of the water samples was aseptically transferred, using a sterilized dropper, into a sterile test tube containing 9ml of the diluent. This gave 10⁻¹ dilution. Subsequently, four fold (10⁻⁴) serial dilutions were prepared from the 10⁻¹ dilution.

Inoculation and Enumeration of Water Samples: 0.1ml

a aliquot of 10⁻⁴ dilution was aseptically removed with a sterile pipette and spread plated with flame sterilized glass spreader on well dried agar plates. This was incubated at 28 ± 2°C for 24hrs. The colonies counted were expressed as colony forming unit per ml.

Total Coliforms (APHA 9216C): About 100ml of the water samples was filtered through membrane filter with the aid of vacuum pump. The filter membrane was placed in the m-HPC agar plate. This was then incubated using an incubator pre-set to 35 ± 5°C for 24hrs. Observation was made for

colony development on the filter membrane. The colonies were then counted as colony forming unit per 100ml.

Fecal Coliforms (APHA 9216D): About 100ml of the water samples was filtered through membrane filter with the aid of vacuum pump. The filter membrane was placed in MacConkey agar plate. This was then incubated using an incubator pre-set to 44.5 ± 2 oC for 24hrs. Observation was made for colony development on the filter membrane. The colonies were then counted as colony forming unit per 100ml.

Table 1: Chemical Analysis of Formation water and Crude Oil Samples

S/N	Parameters	S	T	U	V	W	X	Y	Z
1.	Ph	6.10	9.34	4.54	6.12	4.90	6.45	5.30	7.94
2.	Temperature (°F)	77	182	77	182	77	182	77	182
3.	TDS (mg/l)	120	430	51	78	57	77	73	108
4.	EC (μScm^{-1})	241	850	105	155	115	155	147	218
5.	Colour (PtCo)	10	3	20	10	17	10	15	10
6.	PO_4^{3-} (mg/l)	0.00	1.40	0.00	0.00	0.00	0.00	0.00	0.00
7.	SO_4^{2-} (mg/l)	9.02	6.74	0.05	<0.001	0.08	0.05	2.0	1.05
8.	CL^- (mg/l)	0.10	0.10	<0.001	<0.001	0.01	0.01	0.05	0.05

S= 100% Formation water (77°F), T= 100% Formation water (182°F), U= 100% Crude Oil (77°F), V=100% Crude Oil (182°F),W= 90% Crude oil +10% formation water(77°F), X = 90% Crude oil +10% formation water(182°F), Y = 50% Crude oil +50% formation water(77°F), Z = 50% Crude oil +50% formation water(182°F).

3. Result and Discussion

It was observed from the test result of chemical parameter (table 1) that while most of the parameter showed lower values with crude oil sample, the values were higher with formation water sample. Crude oil at 77°F had TDS OF 5mg/l and 120mg/l for formation water respectively. This could be explained based on the suspended and solid inherent in formation water sample. The electrical conductivity at (77°F) for crude oil 105 (μScm^{-1}) and 241 (μScm^{-1}) for formation water sample. This is a reflection of the concentration of TDS in samples. The higher the concentration of TDS the higher the Electrical conductivity.

Also it was observed that an increase in temperature also increased the concentration of most of the parameter. While TDS was 120 mg/l at 77°F for formation it was 430mg/l at 182°F. This was also seen in crude oil sample result, 51mg/l and 78mg/l at 77°F and 182°F respectively. This could be due to an increase in concentration of the suspended and dissolved solid due to evaporation at higher temperature. The electrical conductivity and pH also followed the same trend.

Table 2 showed that the concentration of most of the heavy metals were negligible or trace in both crude oil and formation water sample. Although the iron concentration in

both crude oil sample and formation water sample reduced from 0.28 to 0.16 and 0.2 to 0.1at 77°F and 182°F respectively. This could be due to oxidation process of the iron metals at elevated temperatures.

Generally it could be observed that all the parameters analysed in both chemical and heavy metal parameters at laboratory temperature were higher in formation water samples than crude oil samples as shown in Table 1 and 2.

Test result indicated (Table 3) that microbiological parameter tested were higher in formation sample than crude oil sample. Total Heterotropic bacterial was 2.6×10^6 cfu/100ml in formation water sample but 2.5×10^2 cfu/100ml in crude oil sample. The Total coliform and Fecal coliform were 70 cfu/100ml and 2.1×10^6 cfu/100ml respectively in formation water sample but 30 cfu/100ml and 2.0×10^2 cfu/100ml in crude oil sample. This could be due to contamination of produced water sample with pollutants and microbes.

Table 2: Heavy metals analysis of Crude oil and Formation water samples

S/N	Parameters	S	T	U	V	W	X	Y	Z
1.	Iron (mg/l)	0.28	0.16	0.2	0.10	0.22	0.19	0.24	0.2
2.	Zinc (mg/l)	0.9	0.00	0.03	0.00	0.05	0.00	0.12	0.00
3.	Manganese (mg/l)	0.002	<0.001	0.00	0.00	0.00	0.00	<0.01	0.00
4.	Arsenic (mg/l)	0.00	0.00	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
5.	Chromium (mg/l)	0.00	0.00	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
6.	Lead (mg/l)	0.00	0.00	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
7.	Cobalt (mg/l)	0.00	0.00	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
8.	Copper (mg/l)	0.00	0.00	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001

S= 100% Formation water (77°F), T= 100% Formation water (182°F), U= 100% Crude Oil (77°F), V=100% Crude Oil (182°F),W= 90% Crude oil +10% formation water(77°F), X = 90% Crude oil +10% formation water(182°F), Y = 50% Crude oil +50% formation water(77°F), Z = 50% Crude oil +50% formation water(182°F).

Table 3: Micro biological Analysis of formation water and Crude oil samples at laboratory Temperature

S/N	Parameters	S	T	U
1.	Total Heterotropic Bacterials (cfu/100ml)	2×10^6	2.5×10^2	1.0×10^2
2.	Total coliform (cfu/100ml)	2.1×10^6	2.0×10^2	10
3.	Fecal coliform (cfu/100ml)	70	30	20

S= 100% Formation water (77°F), T = 100% Crude oil sample (77°F), U = 50% Formation water + 50% Crude oil (77°F)

4. Conclusions

Formation water analysis plays a role in dynamic modelling of reservoirs, quantifying reserves and calculating completion cost. Formation water composition depends on a number of parameters including depositional environment, mineralogy of the formation, its temperature and the influx or migration of fluids. Influx of formation water into crude oil increases the concentration of physicochemical parameters at both laboratory and formation temperature which might be a production concern. Therefore in order to produce high quality crude oil with low level of contaminants, the influx of formation water into crude oil should be controlled at both drilling and production stage. Detailed analysis of the effects on flow properties needs to be carried out as the next step of research.

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