



Evaluation of the Physico-Chemical Properties of Produced Water from Oil Producing Well in the Niger Delta Area, Nigeria

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ABSTRACT: Physicochemical properties of produced water from oil producing well were conducted using standard methods (American standard for testing and materials). Samples were obtained at different periods within two months. Produced water comprises approximately 98% of the total volume of exploration and production (E&P) waste generated by the oil and gas industry. Results obtained; pH (7.90-8.10), total oil and grease (27.00-37.00mg/l), sulphate (45.00-75.00mg/l), total petroleum hydrocarbon (12.00-14.00 mg/l), electrical conductivity (26100.00-26600.00 μ s/cm), total dissolved solid (16750.00-17100.00mg/l); salinity (22801.00 – 23403mg/l) show that all the measured parameters were within specification as recommended by Department of Petroleum Resources (DPR). TOG of produced water receives the most attention in both offshore and onshore locations while salt content (electrical conductivity, salinity and total dissolved solids) receive more attention in onshore locations. TOG and TPH above permissible limit (40 mg/l and 20 mg/l respectively) reduces the biochemical oxygen demand in the sea which is detrimental to the survival of aquatic life. Maintaining sulphate concentration within acceptable limit prevents scale formation by calcium and barium ions. Volume of water produced increases with the age of Crude oil production. ©JASEM

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Produced water also known as oilfield waters can be defined as contaminated water trapped in the reservoir rock and brought up along with oil or gas during production. It is a by-product of the production of hydrocarbons (oil and gas) from underground reservoirs. It consists of formation water, which is water naturally present in the reservoir, or condensed, water in gas production (Huishu Li, 2013). Besides elevated concentration of heavy metals such as barium, uranium, cadmium, chromium, strontium and lead, produced water contains dispersed oil droplets and dissolved organic compounds and significant amount of anion such as carbonate, bromide sulphate (Ayad, *et al.*, 2010). Almost all offshore oilfields produce large quantities of contaminated water that can have significant environmental effects if not handled properly. Over the life of a well, the volume of water produced will exceed the volume of oil by a factor of 3-6 times (Utvik, 2003). The American Petroleum Institute estimates that in stripper oil well operations approximately nine barrels (378 gallons) of produced water are recovered for each barrel of oil. Sources of this water may include flow from above or below the hydrocarbon zone, flow from within the hydrocarbon zone, or flow from injected fluids and additives resulting from production activities. This water is frequently referred to as connate water or formation water and becomes produced water when the reservoir is produced and these fluids are brought to

the surface (API, 2000). Produced water constitutes the largest waste stream from petroleum production operations. They contain chemicals, oil, grease, and sometimes, naturally occurring radioactive materials which could harm the environment. The management of produced water continues to receive attention because of the volume involved, cost of treatment and the potential environmental implications (Breit *et al.*, 1998).

In Nigeria, estimated current average water to oil ratio of 1:1, about one billion barrels of water are disposed annually from oil and gas production operations (Huishu Li, 2013). In the United States, Produced water comprises approximately 98% of the total volume of exploration and production (E&P) waste generated by the oil and gas industry and is the largest volume of waste stream generated by the oil and gas Industry (Khatib and Verbeek 2003). Comparing API's (American Petroleum Institute) Produced water survey conducted in 1985 and 1995 with the report in 2002 it can be demonstrated that the volume of water produced increases with the age of Crude oil production. API calculated a water-to-oil ratio of approximately 7.5 barrels of water for each barrel of oil produced in 1985 and 1995 as against a water-to-oil ratio of approximately 9.5 barrels in 2002 (EPA 2002). For Crude oil wells nearing the end of their productive lives, reports show that water

can compromise as much as 98% of the material brought to the surface (Khatib and Verbeek 2003).

Physicochemical properties can be defined as properties that are influenced by both physical and chemical factors (Mackay and Paterson, 1991). They are physical properties related to interactions with different media, properties or molecular attributes influenced by intrinsic chemical reactivity. Examples are pH, electrical conductivity; total dissolved solid, sulphide and sulphate concentration, total oil and grease, chemical oxygen demand, etc (Jorgensen and Duffy 2002). When mixed with seawater, most physicochemical features of produced water (low dissolved oxygen and pH, elevated salinity and metals) do not pose a hazard to water column biota, but in shallow, turbid waters, elevated concentrations of hydrocarbons may be detected in surface sediments up to about 1,000m from the discharge (Onojake and Abanum, 2012).

This Study is aimed at evaluating the physicochemical parameters of produced water in the Niger Delta area of Nigeria and possible effect on the environment (Offshore location, Shallow waters).

MATERIALS AND METHODS

Produced water was obtained from oil producing well in the Niger Delta area twice at different periods of the month for two non consecutive months. Samples were labeled 1 and 2 for the first month, 3 and 4 for the second month. These samples underwent different treatment before analyses and subsequent discharge to the environment. Further studies will be aimed at understanding different methods of treating Produced water to obtain parameters within specification. Physicochemical parameters such as pH, electrical conductivity, salinity, total oil and grease (TOG), total petroleum hydrocarbon (TPH), sulphate concentration were determined using M220 Mettler Toledor meter, Innolab Conductivity meter, Metrohm Titrator, Fourier transform Infrared Spectrometer and Sensidyne Nephelometer respectively.

pH Determination of Produced Water: The pH meter and associated electrodes were standardized using two reference buffer solutions within the range of the anticipated sample pH. The sample measurement were made under strict controlled conditions and prescribed techniques. The already calibrated electrodes were immersed into the sample. As soon as the electrode output stabilizes, the stability indicator appears displaying the pH and temperature.

Determination of Total Oil and Grease (TOG) in Produced Water: Sample obtained was acidified with

Hydrochloric acid. 25 ml of tetrachloroethylene (TCE) was used to extract the organic portion of the sample. The extract was diluted to 50 ml with distilled water. 25 ml of the organic extract was examined by Fourier transform infrared spectroscopy in water analyzer to measure the amount of Oil and Grease.

Determination of Total Petroleum Hydrocarbon in Produced Water: Sample obtained was acidified with Hydrochloric acid. 25 ml of Tetrachloroethylene (TCE) was used to extract the organic portion of the sample. The extract was filtered through Florisil to remove polar components and then diluted to 50 ml with distilled water. 25 ml of the organic extract was examined by Fourier transform infrared spectroscopy in water analyzer to measure the Total Petroleum hydrocarbon.

Determination of Sulphate Ion in Produced Water: 10ml of standard solution and 10ml of distilled water were added to a 250ml Erlenmeyer flask in addition to 5.0ml of the conditioning reagent and stirred gently. 0.1-0.2g of 20-30mesh BaCl₂ was carefully added to the flask. The Prepared content was poured into the nephelometric cell, and let to stand for five minutes. While waiting, the Nephelometer was zeroed at 420nm with distilled water to obtain the absorbance of the standard. Similar preparation was carried out for the sample. An absorbance versus concentration curve was created with the original concentration of the standard to obtain the sulphate concentration in the sample.

Determination of the Electrical Conductivity of Produced Water: The Conductivity meter was calibrated with the appropriate buffer solution. The probe from the already calibrated conductivity meter was immersed into the beaker containing the sample. Time was allowed for the conductivity meter to gain stability then conductivity recorded.

Determination of the Salinity of Produced Water: 1 ml of the sample was made up to 20 ml using distilled water. 1 ml of potassium dichromate indicator was added. Titrate with a silver nitrate solution until color changes to brick red. Titration was achieved using a combined ring silver coated electrode. Salinity is calculated using the equation:

$$\text{Salinity} = \frac{A \times N \times 58.5 \times 1000}{\text{Vol. of Sample}}$$

A = Vol. of Silver Nitrate

N = Molarity of Silver Nitrate

RESULTS AND DISCUSSION

Table - 1, Physiochemical Properties of Produced Water From Oil Producing Well

Parameter	1st Month		2nd Month		EGASPIN SPEC.
	Sample 1	Sample 2	Sample 3	Sample 4	
pH	7.94	8.02	8.10	8.05	6.50 - 8.50
TOG (mg/l)	30.00	27.00	37.00	32.00	40.00
Sulphate (mg/l)	55.00	45.00	75.00	40.00	200.00
TPH (mg/l)	12.00	14.00	14.00	13.00	20.00
Conductivity ($\mu\text{s}/\text{cm}$)	26200.00	26600.00	26100.00	26500.00	No limit
TDS (mg/l)	16760.00	17020.00	16750.00	17100.00	No limit
SALINITY (mg/l)	23002.00	23403.00	22801.00	23315.00	No limit

Sample temperature was maintained between 20.0 to 23.2 °C. Results are averages obtained from multiple measurements and are validated using the standard deviation of each parameter. The Physicochemical properties of produced water vary considerably depending on the geographical 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 in other words, produced water from the same well as considered in this study tend to possess physicochemical properties within the same range at different period of time as shown in Table 1. (Stephenson, 1992).

The pH of produced water usually is controlled by the CO₂/bicarbonate system. Because the solubility of CO₂ is directly proportional to temperature and pressure, the pH measurement should be made in the field if a close-to-natural-conditions value is desired (Ali *et al.*, 1999). The pH of the water is not very useful for water identification or correlation purposes, but it does indicate possible scale-forming or corrosion tendencies of a particular water (Breit *et al.*, 1998). The pH also may indicate the presence of drilling-mud filtrate or well-treatment chemicals. Organic acids, such as acetic acid, also can control the pH (Johnsen *et al.*, 2004). Results obtained from Table 1 shows that the pH of produced water obtained within the period under review meet EGASPIN Specification (6.5 -8.5). EGASPIN (Environmental Guideline and Standard for Petroleum Industries in Nigeria) is an arm of DPR (Department of Petroleum Resources) (EGASPIN, 2000). Reduced pH can affect the oil /water separation process and can impact receiving waters when discharged. It can also obstruct the oil / water separation process (Breit *et al.*, 1998).

Oil and grease does not constitute a single chemical compound but a measure of many different types of organic material that respond to a particular

analytical procedure (Faksness *et al.*, 2004). Different analytical methods measure different organic fractions. The specific analytical method used is therefore important in determining the amount of oil and grease (Ali *et al.*, 1999). There are different constituents of oil and grease. Even with the same oil and grease content, not all produced water contain the same constituent of oil and grease (Viel, 2011). Oil and grease is made up of at least three forms namely; Free oil which are large droplets easily removed by gravity separation method, Dispersed oil in the form of small droplets which are more difficult to remove and Dissolved oil which are hydrocarbons and other similar materials that are challenging to remove (Faksness *et al.*, 2004). If the dispersed oil contacts the ocean floor, contamination and accumulation of oil on ocean sediments may occur which can adversely affect the benthic community. Dispersed oils can also rise to the surface and spread causing sheening and increased biological oxygen demand near the mixing zone (Stephenson, 1992). Factors that affect the concentration of dispersed oil in produced water include oil density, interfacial tension between oil and water phases, type and efficiency of chemical treatment and type, size and efficiency of the physical separation equipment (Ali *et al.*, 1999). Table 1 shows that the TOG of the produced water samples obtained (27.00-37.00mg/l) were all within acceptable standard (40.00mg/l) (EGASPIN, 2000; EPA 2002).

Below is a table showing the average monthly and daily acceptable TOG of produced water permitted by several Countries for ocean disposal.(Viel, 2011).

Table 2: Acceptable TOG (mg/l) for Produced Water Permitted by Several Countries for Ocean Disposal

Country	Monthly Average	Daily Maximum
Canada	30	60
USA	29	42
Ospar (NE Atlantic)	30	-
Mediterranean Sea	40	100
Western Australia	30	50
Nigeria	40	72
Brazil	-	20

Petroleum hydrocarbons are organic chemicals consisting of just carbon and hydrogen, they are the chemical of greatest environmental concern in produced water (Terrens and Tait, 1996). Petroleum hydrocarbons are classified into two groups: saturated hydrocarbons and aromatic hydrocarbons. The most abundant hydrocarbons in produced water are the one-ring aromatic hydrocarbons, benzene, toluene, ethylbenzene, and xylenes (BTEX) and low molecular weight saturated hydrocarbon (Frost *et al.*, 1998). They also contain Polycyclic hydrocarbons which are hydrocarbons containing two or more fused aromatic rings (Stephenson, 1992). The solubility of petroleum hydrocarbons in water decreases as their size (molecular weight) increases, aromatic hydrocarbons are more water-soluble than saturated hydrocarbons of the same molecular weight (Ayad *et al.*, 2010). The hydrocarbons in produced water appear in both dissolved and dispersed (oil droplets) form (Frost *et al.*, 1998). Due to the fact that petroleum hydrocarbons are many, it is not usually practical to measure each one individually. However, it is useful to measure the total amount of all hydrocarbons found together in a particular sample of soil, water, or air (Khatib and Verbeek 2003). Owing to the high volatility of BTEX, they are easily lost during produced water treatment by air stripping and during initial mixing of the produced water plume in the ocean (Terrens and Tait, 1996). Polycyclic hydrocarbons on the other hand are of greatest environmental concern in produced water because of their toxicity and persistence in the marine environment. Owing to the low aqueous solubility of Polycyclic hydrocarbons, they are associated primarily with dispersed oil droplets (Faksness *et al.*, 2004; Johnsen *et al.*, 2004). Generally, the concentration of organic compounds in produced water increases as the molecular weight of the compounds increases (Ayad *et al.*, 2010). The lighter weight compounds (BTEX) are less influenced by the efficiency of the oil/water separation process than the higher molecular weight polycyclic hydrocarbons hence are not measured by the Oil and grease analytical method (Khatib and

Verbeek 2003). Polycyclic hydrocarbons when present in water increases the biological oxygen demand and are highly toxic to aquatic organisms (Faksness *et al.*, 2004). When TPH is released directly to water, certain TPH fractions will float in water and form thin surface films. Other heavier fractions will accumulate in the sediment at the bottom of the water, which may affect bottom-feeding fish and organisms (Ali *et al.*, 1999). Some organisms found in the water (primarily bacteria and fungi) may break down some of the TPH fractions.. Aromatic hydrocarbons and alkylated phenols are the most important contributors to toxicity (Terrens and Tait, 1996). Alkylated phenols are considered endocrine disruptors, however phenols and alkyl phenols can be readily degraded by bacterial and photo-oxidation in seawater and marine sediments (Frost *et al.*, 1998; Stephenson, 1992). Table 1 shows that the measured TPH (12.00-14.00 mg/l) of the samples obtained were within acceptable limit (20 mg/l). (EGASPIN, 2000; EPA 2002)

The salt content of Produced water is measured in terms of the Conductivity, Total dissolved solid and salinity. These parameters are not given much attention as TOG and TPH as far as offshore operations are concern, owing to the fact that the salt content of produced water from the oil well considered in this study constitutes a minute fraction of the salt content of the sea which is > 4 Siemens. The sea which is the receiving environment for offshore locations have a high tolerance level for salt content (Conductivity, TDS and Salinity) (Breit *et al.*, 1998)

Sulphate concentration controls the solubility of several other elements in solution particularly Barium and Calcium. Table 1 shows that the Sulphate concentration of the samples analyzed (40.00 – 75.00 mg/l) meet EGASPIN and USEPA specification for offshore locations (Shallow waters). When the Sulfate Concentration in Produced water is low, it allows the formation of high concentration of Barium and Calcium ions in solution thereby reducing the likelihood of producing large amounts of Barium and Calcium scales (Ayers and Parker, 2001).

Conclusion: All the physicochemical parameters for produced water determined in this study fell within acceptable standard (DPR and USEPA specification). The basic difference between TOG and TPH is more on the analytical method employed in the determination (constituents involved) than in the form in which they appear. Physicochemical parameters are key indicators that express the level of contamination in produced water.

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