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Physico-Chemical Consequences of Industrial Water Discharge on Marine Structures in Escravos and Focados Waters in Warri, Delta State

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Abstract

Globally, there is no doubt that creatures and manmade structures are under terrific danger occasioned by undesired alterations in the physical, chemical and biological characteristics of air, water and soil due to increased industrial activities. The study therefore looks at the effect of industrial associated produced water on marine structures in Escravos and Focados waters in Warri, Delta state. The study identified oil and gas exploration activities in the area and the release of produced water by oil and gas extraction companies as a major cause of corrosion of marine structures in the study area. The study sought to determine the iron and chlorine parameter in post treated produced water as it affect corrosion of offshore structures in Escravos and Focados water in Warri, Delta State. Three hypotheses were formulated in line with the objectives of the study. The results of the analysis showed the physico-chemical properties of produced water as having pH (6.25-6.40), chloride (15,679-16,334.21mg/l) and total dissolved solids-TDS (31,400.00-31,430mg/l). These did not meet the DPR standards for disposal offshore and therefore requires further treatment to bring these parameters within allowable limits. The study also showed that produced water have potential impacts on the recipient environment depending on where it is being discharged.

Keywords: *Produced Water, Physico 0- chemical, Heavy metals, Marine Structures*

1.0 Introduction

Oil extraction as well as maritime transportation in the Niger Delta is an ongoing activity since the 1950s and Nigeria exports around 15 million tonnes of oil every day, ranking one of the top 15 exporters in 2009 and oil exports accounts for 95 % of the foreign exchange earnings and 80 % of the budgetary revenues (Olof and Jonas, 2015), the oil pollution has adversely affected the dredging and other maritime related activities in the area. Produced water is the major waste product generated from petroleum exploration and production activities. Others include spent drilling muds, and drilling cuttings. Produced water is known to be a complex composition of numerous hazardous chemicals, including large quantities of heavy metals, inorganic, and organic substances, including naturally occurring radioactive materials (NORMs), Veil & Clark, (2010). According to Telleza, Nirmalakhandan and Gardea (2002), the two main disposal methods for produced water are environmentally unfriendly. The array of hazardous chemicals contained in petroleum waste streams and their unwholesome disposal has resulted in untold damage to environmental media that are unyielding to known remediation technologies.

Corrosion of marine structures are caused by produced waters on both inland waterways and on the ocean, they are majorly contributed during the course of offshore oil and gas exploration and production as well as shipping routine activities, Olukayode (2015). Sometimes the problems may even originate majorly from routine discharges of oily bilge and ballast water from marine shipping; dumping of non-biodegradable solid waste into the ocean; accidental spills of oil, toxics or other cargo or fuel at ports and while underway; air emissions from the vessels' power supplies; port and inland channel construction and management; and ecological damage in consequence of the introduction of outlandish species transported on vessels Onyema, Iwuanyanwu, and Emeghara (2015), (Organisation for Economic Cooperation and Development, OECD 1997). The degree of availability of marine reception facilities are minute in most vessels and in various seaports in Nigeria and in West and Central African ports hence ship waste collection processes in the ports are not only inefficient but also their management remains poor, Onwuegbuchunam, Ebe, Okoroji, & Essien, (2017). Oil and Gas Institute (2019) identified corrosion on vessels and marine structure as one of the major effects of oil pollution. Against this background, this research empirically established the level of oil pollution from the produced waters and through laboratory analysis determine the content of post treated produced water discharge and their impact on marine structures by comparing the standards of the parameters to regulatory standard of DPR. The aim of this research is to analyse the impact of produced water on corrosion of marine structures in Escravos and Focados waters in delta state. The study will further be focusing on establishing the incidence of oil pollutants and determining the iron (corrosive substance) parameter content in post treated produced water in Delta waters of Escravos and Focados and determining chloride (corrosive substance) parameter content in post treated produced water in Delta waters of Escravos and Focados.

1.0 Materials and Methods

The research design selected for this study is based on the focus of the study as indicated in the objectives of the research. One of the research strategies that was adopted was conducting multiple locations studies or sample experiment of water samples in Escravos water and Forcados in Delta State, Nigeria relative to the DPR.

Associated water was collected at Exploration and Production (E&P) sites at two different periods between the study periods.

Associated water samples from E&P sites were subjected to clinical test analysis to ascertain the incident and level of pollution relative to DPR standards. For results on tables 4.1 and 4.2, Sampling points were watchfully selected to obtain samples that are truly representatives of the post-treated produced water. Samples were collected with sterile 1000 liters Wheaton glass bottles from flowing effluent at the point of final discharge to the receiving water at an interval of two weeks.

Instruments used for analysis include DspH-3, pH/conductivity meter, OAKTONTDS meter, YSI 550A dissolved oxygen meter and Gun-type infra-red thermometer. All laboratory analyses were carried out in Dukoria laboratory at Warri Sapele road, Warri Delta State according to standard methods as described in EGASPIN (Environmental Guidelines and Standards for the Petroleum Industry) (2002) and Federal Environmental Protection Agency, FEPA, (1991) guidelines; APHA-AWWA-WPCF (1998) and the annual book of ASTM standards, (ASTM, 2002) were used without modifications for the appropriate analyses. In addition, all laboratory procedures were adequately standardized and all instruments appropriately calibrated.

The following parameters were analyzed; turbidity, TSS, THC, BOD, COD, Salinity and trace metals. For pH, the pH meter was standardized with buffer solution and calibrated before measurement. For Turbidity, the Jackson candle turbid-meter was set up. Sample was poured from a measuring cylinder into the calibrated glass tube of the turbid-meter. The beam of light from the candle was then observed until the samples cloudiness impelled the light. The reading on the glass tube was done and converted into Jackson candle units.

Oil and Grease Content Determination

The gravimetric method was used. 100ml of water sample was measured and poured into the separation funnel. 10ml of toluene was measured and poured into the separating funnel containing sample. The two reagents were mixed together thoroughly by shaking for some minutes. The mixture was then allowed to stand for some minutes during which the toluene attracted to oil and grease in the sample to the top of the liquid in a layer. The funnel top was then opened and the water ran-off leaving the oil layer behind. The oil left behind was then dried and the water sample was then reweighed and the difference in weight before and after separation gave the oil and grease content.

Calcium Content Determination

Calcium content was determined using titration method. 50ml of the sample was measured and transferred into a beaker then 2.0 drops of indicator and 2.0ml of buffer solution (NaOH) were added to the sample, and thoroughly stirred. The burette was filled to zero position with ETDA and then titrated against the sample mixture until the end point was reached when the muroxide indicator changed colour from pink to violet. The ion concentration was calculated as follows:

1000 x Volume of ETDA x N = Volume of sample…………………… (1)
Ca^{2+} (mg/1)

Where, N = Normality of sample

Chlorine Content Determination

Chlorine ion content was determined using the Mobr's method. 50ml of the sample was measured into a beaker and the dilution factor was noted. The sample was adjusted to a pH of 8.3 by the use of standard sodium hydroxide. 5% of potassium chromate was also added to the sample. The burette was then filled with 0.01ml silver nitrate to zero point, and titrated against the sample. When the endpoint was reached, chlorine ion concentration was obtained from the formula:

(M1 x N) $AgNO_3$ x 35500 x 10= M1 sample ……………………….. (2)
Cl^-(mg/L)

Iron Content Determination

For iron content determination, 100ml of sample was measured into a beaker. The reagent was then gently injected into the sample with the aid of a syringe. The colour of the sample was observed until the colour change was fixed even with the injection of more ortho-phenanthroline. A standard colour chart was then used to determine the concentration of Iron in the sample. Concentrations of heavy metal ions were determined using the Atomic Absorption Spectrophotometer (Perkin Elmer 5100PC). The summary of various parameters and the methods used for analyses are as shown in Table 1.

Table 1: Instruments of Chemical Analysis

Parameter	Method of analysis
pH	pH meter
Turbidity, copper, lead, nickel	Turbidimetry
Specific gravity	Hydrometer
Oil and grease content, sodium,	Gravimetry
Potassium, calcium, iron, zinc, chloride, magnesium, sulphate, carbonate, bicarbonate ions	Titration
Barium, strontium	Atomic absorption spectro-photometry
Suspended solid	Gravimeter (Membrane Filter)
Dissolved solid	Titration
Particle shape	Electron microscope
Temperature	Thermometer

DPR, 1991

T- Test Analysis

Results from the laboratory test were compared to the DPR standards as adopted from the UK indices as the best international practices using the T-Test analysis. The T-test assesses whether the means of two groups are statistically different from each other. The formula for T-test is a ratio. The top part of the ratio is just the difference between the two means or average. The bottom part is a measure of the variability or dispersion of the scores. The formula is essentially another example of the signal to noise metaphor in research. The difference between the means is the signal that, in this case, we think our program or treatment introduced into the data; the bottom part of the formula is a measure of variability that is essentially noise that may make a harder to see the group difference. X_t-X_c

The formula is given below:

$$\frac{Signal}{Noise} = \frac{Difference\ btween\ group\ means}{Variability\ of\ groups}, \qquad \text{T-Value} = \frac{Xt - Xc}{SE(Xt - Xc)}$$

The top part is easy to compute; just find the difference between the means. The bottom part is called the standard error of the difference.

To compute it, we take the variance for each group and divide it by the number of people in that group. We add these two values and then take their square root.

The specific formula is given below;

$$SE(X_T - X_C) = \sqrt{\frac{VarT}{NT} + \frac{Varc}{Nc}}$$

Formula for standard error of the difference between the means.

Remember, the variance is simply the square of the standard deviation.

The final formula for the T-Test is shown below:

$$T = \frac{XT - XC}{\sqrt{\frac{VarT}{NT} + \frac{Varc}{Nc}}}$$

The test will be positive if the first means is larger than the second and negative if it is smaller. Once you compute the T-test value, you have to look it up in a table of significance to test whether the ratio is larger enough to say that the difference between the groups is not likely to have been a chance finding.

Decision Rule

When compared the calculated value of T-test and the value on the contingency table, the decision rule is as follows:

Accept null hypothesis (H_o) if T-test value is larger than or equal to critical value $t_{\alpha,}$ and vice versa. Where α is level of significance which is taken to be 0.05

Results and Discussions

Table 4.1: DPR standard for Produced Water Discharge

Parameters	Unit	DPR Limit
Date sampled		
pH	-	6.5-8.5
Temperature	˚C	30.0
THC	mg/L	40.0
Chloride	mg/L	2000.0
Turbidity	mg/L	15.0
TDS	mg/L	5000.0
TSS	mg/L	50.0
COD	Mg/L	125.0
BOD	Mg/L	125.0
Lead	Mg/L	
Iron	Mg/L	
Copper	Mg/L	
Chromium	Mg/L	0.5
Zinc	Mg/L	5.0

Source: DPR 1991/99

Table 4.2: The Physical, Chemical, and Biological Characteristics of the Post –treated Produced Water.

Parameters	**Unit**	**Week 1**	**Week 2**	**Mean**	**SD**
Date sampled		19/07/14	27/07/14		
pH	-	6.25	6.40	6.33	0.11
Temperature	OC	29.50	29.75	29.75	0.36
THC	mg/L	17.31	13.00	15.16	3.05
Chloride	mg/L	15,679.40	16,334.21	16,006.81	463.02
Turbidity	mg/L	10.70	11.00	10.85	0.9
TDS	mg/L	31,430.00	31,400.00	31,415.00	21.21
TSS	mg/L	10.0	12.00	11.00	1.41
COD	Mg/L	95.33	92.10	93.72	2.28
BOD	Mg/L	61.25	64.30	62.78	2.16
Lead	Mg/L	0.004	0.002	0.003	0.001
Iron	Mg/L	0.630	0.659	0.645	0.021
Copper	Mg/L	0.084	0.077	0.080	0.005
Chromium	Mg/L	0.005	0.007	0.006	0.001
Zinc	Mg/L	0.166	0.173	0.170	0.005

Source: Results of the experiment

Table 4.3: The Physical, Chemical, and Biological Characteristics of the Recipient Water.

Parameters	**Units**	**North**	**South**	**Central**	**East**	**West**
pH	-	8.14	8.20	7.41	8.27	8.35
Temperature	OC	29.3	29.3	30.2	29.5	29.0
Conductivity	ms/cm	34.1	33.9	40.0	34.2	43.7
THC	mg/L	<0.01	<0.01	0.10	0.03	<0.001
TOC	mg/L	5.43	5.50	6.91	5.11	5.0
DOC	mg/L	4.8	4.6	4.0	4.9	5.2
BOD	mg/L	46.2	47.11	60.1	47.04	47.0
COD	mg/L	60.18	59.39	72.01	61.0	61.41
TDS	mg/L	36,337	36,300	36,500	36,510	36,400
Chloride	mg/L	20,105	20,110	21,420	20,218	20,228
Turbidity	mg/L	7.00	6.87	8.00	7.00	6.50
Phenols	mg/L	0.01	<0.01	0.02	0.02	<0.01
Cyanide	mg/L	0.002	0.004	0.006	0.005	0.001
Ammonium	mg/L	4.906	4.970	6.118	4.600	4.613
Nitrate	mg/L	0.230	0.228	0.126	0.201	0.230
Nitrogen	mg/L	1.400	1.404	1.300	1.355	1.326

Phosphorous	mg/L	0.035	0.042	0.050	0.046	0.040
Arsenic	mg/L	0.002	0.003	0.004	0.0002	0.001
Lead	mg/L	< 0.001	<0.001	0.003	0.001	0.001
Zinc	mg/L	0.230	0.220	0.225	0.226	0.215
Chromium	mg/L	<0.001	<0.001	0.008	<0.001	<0.001
Nickel	mg/L	<0.001	< 0.001	<0.001	<0.001	<0.001
Vanadium	mg/L	< 0.001	< 0.001	<0.001	<0.001	<0.001
E-coil	MPN/100Ml	37.00	41.00	56.0	41.00	38.00

Produced Water

Results of the analyses of the physico-chemical properties of produced water are shown in Table 4.1. The pH (6.25-6.40), chloride (15,679-16,334.21mg/l) and total dissolved solids-TDS (31,400.00-31,430mg/l). These did not meet the DPR standards for disposal offshore and therefore requires further treatment to bring these parameters within allowable limits.

Recipient Water

Results of the analyses or the physico-chemical parameters of the recipient marine water from five designated points to the effluent plant (North, South, Central, East and West), is shown in Table 4.3. Total Hydrocarbon Content, THC (13.00-17.31mg/l), turbidity (10.70-11.00mg/l), total suspended solids, TSS (10.00-12.00mg/l), and temperature (29.50-29.75^{o}C), all fall within the DPR allowable limits and therefore do not constitute any treat to the recipient marine environment. This was also the case of the chemical oxygen demand, COD (92.10-95.33mg/l), biochemical oxygen demand, BOD (61.25-64.30mg/l), and heavy metals of lead, iron, copper, chromium, and zinc. The pH of the recipient marine water showed compliance with the DPR standards unlike that of the produced water with a mean value of 6.33. The central discharge point with a pH value of 7.41 indicates the point maximum concentration of the effluent discharge thereby having a near neutral pH. The total hydrocarbon concentration (THC) was 0.1mg/l at the central discharge point. The North, South, East, and West points had values of 0.01mg/l, 0.01mg/l, 0.03mg/l, and 0.01mg/l. This gives the following implications:

- THC emanates from a source and enters the recipient water.
- THC entering the recipient water emanates from the central discharge point.
- The source concentration is higher than other points.
- The recipient water at the east point is slightly affected.

The dissolved oxygen content (DOC) values show a non-compliance with DPR standards. The total dissolved solid (TDS) also show a level of non-compliance with DPR standards.

Other parameters such as nitrate, ammonium ion, cyanide, phosphate, phenols, *E. coli*, and trace metals showed compliance with DPR standards.

In all the physico-chemical parameters evaluated, the central discharge point showed slight variations in value showing that this was the point of maximum concentration before dilution with distance from the discharged point.

It is obvious that produced water have potential impacts on the recipient environment depending on where it is being discharged. For example, discharges to small streams are likely to have a larger environmental impact than discharges made to the open ocean by virtue of dilution that takes place there.

Table-4.4 Chemical analysis of produced water in Forcados and Escravos oil field terminal

Parameter	Allowed limits	Terminals		Station Flow		
		Forcados	Escravos	A	B	C
pH @75°F	6.5-8.5	8.12	8.53	7.88	8.10	8.43
Resistivity @69°F	0.45	0.68	1.58	0.37	8.40	
Oil/Grease content (Mg/l)	10	55.0	42.0	64	80	40
Copper Mg/l	1	0.25	0.01	0.37	0.44	0.08
lead Mg/l	0.05	0.05	0.03	ND	ND	0.04
Iron, Mg/l	1	0.80	0.95	0.75	0.97	1.16
Nickel Mg/l	1	0.50	0.49	0.54	0.33	0.65
Barium Mg/l	-	16.0	8.00	5	20	11
Zinc Mg/l	1	0.10	1.80	0.98	0.09	0.85
Magnesium Mg/l	-	56.0	34.4	165	4.86	14.75
Chloride Mg/l	600	5100	2583	3589	4678	3970
Sulphate Mg/l	200	12.0	2.0	-	-	38
Carbonate	-	16.0	220	200	180	110
Bicarbonate Mg/1	-	2000	980	4720	1036	710
Total dissolved solid	2000	9000	3978	5300	6850	6440
Total suspended solid	30	60	80	138	104	94
BOD (mg/l)	10	500	8.5	4.5	8.68	5.33
Discharge Temp. °F		85	84	92	85	82

For the results in table 4.4, the method below was used to achieve the results.

Samples of produced water were obtained from three flow stations: A (onshore), B (Swamp) C (offshore) and two terminals (near shore) in the Delta State. Measurement of temperature and pH were done at the sampling point due to sensitivity of their values, while the analysis of other parameters was done in the laboratory.

From table 4.4, results of the effluent water analysis show that the pH of the effluents from the terminals (Focados and Escravos) and flow stations are all within the limit of 6.5-8.5. Similarly, the iron concentration in the effluents from the terminals (Focados and Escravos) and flow stations A and B is within limits. The iron concentration of the effluent from C is high and suggests possible corrosion in the system. However, oil and grease contents of the effluents from all the terminals and flow stations are all above the recommended discharge limit. This is particularly worrisome considering the effects of oil or grease on the environment. Similarly, the Chloride ion**,** total dissolved solids and total suspended solids in all the effluents exceed set limits. The concentration of the total dissolved solids which include heavy metals and dissolved salts, might have been reduced by the installation of proper treating facilities. The high total suspended solid concentrations suggest that the floatation units are not very effective in handling the high volumes of effluent water at the terminals. At the flow stations there were no flocculation units for treating water.

From the above, it can be deduced that the following reactions takes place in the system

Galvanic or Electrochemical or Wet Corrosion Theory

Case 1: Evolution of Hydrogen

At the Anode; $Fe \longrightarrow Fe^{++} + 2e^-$ (Oxidation)

At the Cathode; the hydrogen ions (H^+) are formed due to the acidic environment and the following reaction occurs in the absence of oxygen.

$2H^+ + 2e^- \longrightarrow H_2 \uparrow$ (reduction)

The overall reaction becomes

$Fe + 2H^+ \longrightarrow Fe^{+2} + H_2$

Case 2: Absorption of O_2

This reaction takes place in the presence of Oxygen in basic or neutral medium. The oxide of iron covers the surface of the metal.

At the Anode,

At the Anode; $Fe \longrightarrow Fe^{++} + 2e^-$ (Oxidation)

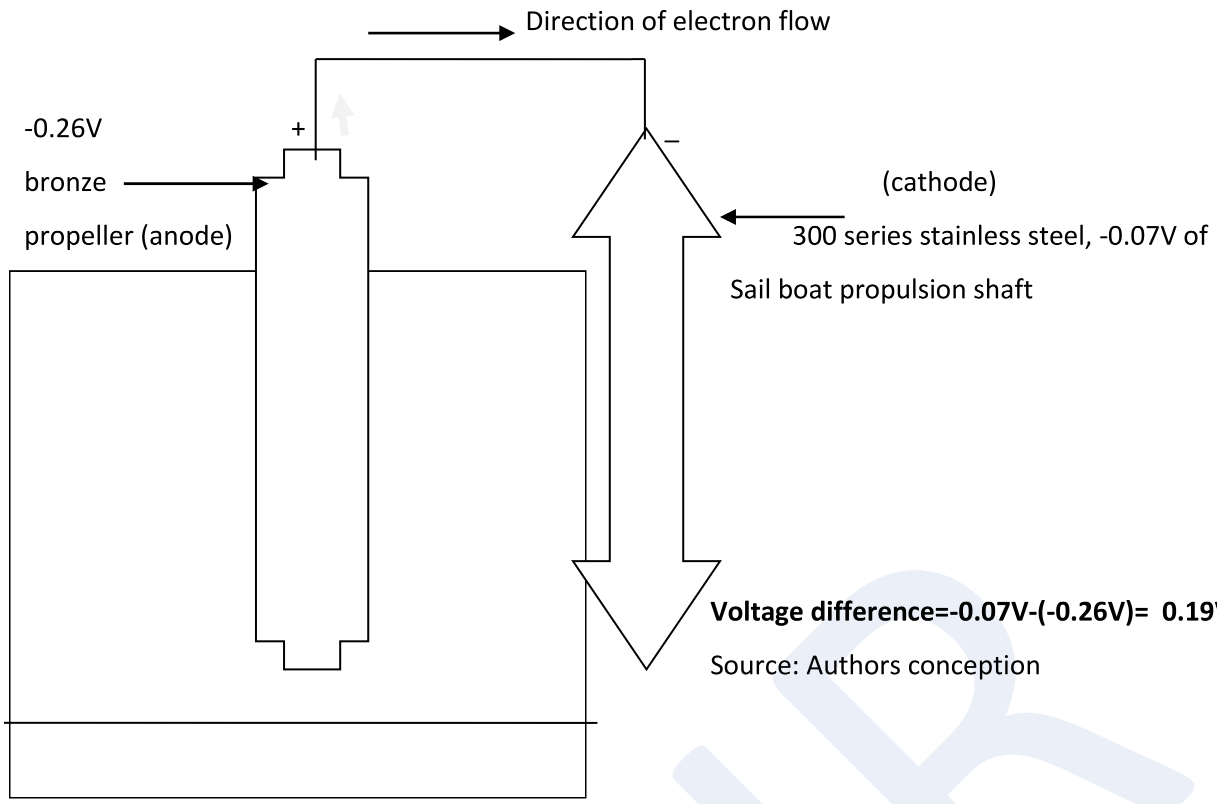
At the cathode

$O_2 + H_2O + 2e^- \longrightarrow 2OH^-$ (reduction)

The overall reaction becomes

$Fe + O_2 + H_2O \longrightarrow Fe^{++} + 2OH^-$ or $Fe(OH)_2$

Figure 2: a simple corrosion model



Voltage difference=-0.07V-(-0.26V)= 0.19V

Source: Authors conception

Test of Hypotheses H_{O1}

$H_{O1:}$ The oil pollutants (oil/grease) content in the Escravos and Focados waters in Delta State are not within the regulatory standards of DPR.

SAMPLE	PARAMETER	STANDARD	DIFFERENCE(D)	D- Ď	(D- Ď)^2
Focados	55	10	45	-1.2	1.44
Escravos	42	10	32	-14.2	201.64
A	64	10	54	7.8	60.84
B	80	10	70	23.8	566.44
C	40	10	30	-16.2	262.44
			Σ(D) 231		Σ(D- Ď)^2 1092.8

Mean difference score (Ď) = $\sum \frac{(D)}{N}$,

Ď=$^{231}/_{5}$, Ď=46.2

Standard deviation of the difference scores: SD=$\sqrt{\frac{\Sigma(D-\check{D})2}{N-1}}$,

$SD = \sqrt{\frac{1092.8}{5-1}} = \sqrt{\frac{1092.8}{4}}$, SD= 16.529

Standard error of the mean of the difference scores, $S\check{D} = \frac{SD}{\sqrt{N}}$

$S\check{D} = \frac{16.529}{\sqrt{5}} = 7.392$

Note: The hypothesized difference between the two conditions is zero, μ_D (hyp)=0

$T = \frac{\check{D}}{S\check{D}}$, $t = \frac{46.2}{7.392}$, t=6.25

Degree of freedom d.f = N-1, 5-1. D.f=4,

From table of critical values at p=0.05 significant level for a two tailed test is 2.87. Our t-value (from the experiment) was 6.25. For this to be significant, it must be greater than the critical t-value.

Degree of Freedom (d.f) = (r-1), Level of significance = 5% = 0.05

The critical value $t_{(tab)} = t_{(0.05)}(4)=2.87$, $t_{(tab)}<t(cal)$: ie, 2.87<6.25

Therefore, it can be concluded that the result is significant and that oil pollutants (oil/grease) content in the Escravos and Focados waters in Delta State are not within the regulatory standards of DPR, the researchers therefore accepted the null hypothesis.

Test of Hypotheses Ho₂

H_{02}: The Iron content of post treated produce water of Escravos and Focados is not within the regulatory standard.

SAMPLE	PARAMETER	STANDARD	DIFFERENCE(D)	D- Ď	$(D-\check{D})^2$
Focados	0.80	1.00	-0.20	-0.08	0.0064
Escravos	0.95	1.00	-0.05	-0.07	0.0049
A	0.99	1.00	-0.01	-0.11	0.0121
B	0.97	1.00	-0.03	-0.09	0.0081
C	1.16	1.00	0.16	-0.28	0.0784
			Σ(D) = -0.12		$\Sigma(D-\check{D})^2 = 0.1099$

Mean difference score (Ď) = $\sum \frac{(D)}{N}$,

$\check{D} = 0.1099/5$, Ď=0.022

Standard deviation of the difference scores: $SD = \sqrt{\frac{\Sigma(D-\check{D})2}{N-1}}$,

$SD = \sqrt{\frac{0.1099}{5-1}} = \sqrt{\frac{0.1099}{4}}$, SD= 0.164

Standard error of the mean of the difference scores, SĎ = $\frac{SD}{\sqrt{N}}$

SĎ = $\frac{0.022}{\sqrt{5}}$ = 0.0098

Note: The hypothesized difference between the two conditions is zero, μ_D(hyp)=0

T =$\frac{Ď}{SĎ}$, t= $\frac{0.022}{0.0098}$, t=2.245

Degree of freedom d.f = N-1, 5-1. D.f=4,

From table of critical values at p=0.05 significant level for a two tailed test is 2.87. Our t-value (from the experiment) was 2.245

For this to be significant, it must be greater than the critical t-value.

Degree of Freedom (d.f) = (r-1), Level of significance = 5% = 0.05

The critical value $t_{(tab)} = t_{(0.05)}$(4)=2.87, $t_{(tab)}$<t(cal): ie, 2.87 > 2.245

Therefore, it can be concluded that the result is significant and Iron content of post treated produce water of Escravos and Focados are within the regulatory standard and global best practices. The researchers therefore rejected the null hypothesis.

Test of Hypotheses H_{O3} (CL^-)

H_{03}: The Chloride content of post treated produce water of Escravos and Focados is not within the regulatory standard.

SAMPLE	PARAMETER	STANDARD	DIFFERENCE(D)	D- Ď	(D- Ď)^2
Focados	5100	600	4500	1116	1245456
Escravos	2583	600	1983	1401	1962801
A	3589	600	2989	395	156025
B	4678	600	4078	694	481636
C	3970	600	3370	-14	196
				Σ(D) 16920	Σ(D- Ď)^2 3846114

Mean difference score (Ď) = $\sum\frac{(D)}{N}$,

Ď=$^{16920}/_{5}$, Ď=3384

Standard deviation of the difference scores: SD=$\sqrt{\frac{\Sigma(D-Ď)2}{N-1}}$,

SD= $\sqrt{\frac{3846114}{5-1}}$ = $\sqrt{\frac{3846114}{4}}$, SD= 980.58

Standard error of the mean of the difference scores, SĎ = $\frac{SD}{\sqrt{N}}$

SĎ = $\frac{980.58}{\sqrt{5}}$ = 438.53

Note: The hypothesized difference between the two conditions is zero, μ_D(hyp)=0

T =$\frac{\check{D}}{S\check{D}}$, t= $\frac{3384}{438.53}$, t = 7.717

Degree of freedom d.f = N-1, 5-1. D.f=4,

From table of critical values at p=0.05 significant level for a two tailed test is 2.87. Our t-value (from the experiment) was 7.717.

For this to be significant, it must be greater than the critical t-value.

Degree of Freedom (d.f) = (r-1), while significance= 5% = 0.05

The critical value $t_{(tab)} = t_{(0.05)}(4)$=2.87, $t_{(tab)}$<t(cal): ie, 2.87<7.717

Therefore, it can be concluded that the result is significant and that the Chloride content of post treated produce water of Escravos and Focados is not within the regulatory standard. The researchers therefore accepted the null hypothesis.

Conclusion/ Recommendations.

From the results of this research, the researcher concludes that Produced water discharged into the environment in the Escravos and Focados Delta State is yet to meet set standards for disposal as concentration of oil/grease content, total dissolved solids, total suspended solids and some other parameters are very high, and not within the stipulated standard. However, the content of ferrous metal is still within the acceptable limit.

Chloride concentration in the waters are so high that it could react with water to form sufficient acid (HCL) which will in turn react or attack the metallic ions or anions at the anode (marine structures, hence corroding the entire system.

Anode; Fe $\longrightarrow$ Fe^{++} + $2e^-$ (Oxidation) thereby

At the cathode

Therefore, the vessels and other marine structures are liable of corroding easily because of the presence of cathode ions and which are highly electronegative.

- Oil Exploration and Production companies should practice or introduce produce water reinjection techniques as a way of environmental protection method. This will also help them in production efficiency by increasing the reservoir pressure for optimal oil production.
  There should be improved regular routine marine structure check practice technique by oil companies and shipping companies for the safety of marine structures.

To reduce toxicity in the system, there should be medium and long-term strategies and guidelines in place to achieve continuous reduction in permissible discharges until zero discharge is achieved.

Ship builders should ensure that more anodic protection metals like aluminum alloys, zinc, magnesium or use of impressed Current, Galvanic Sacrificial Anode, Galvanic Zinc Application, for corrosion control.

DPR should also undertake not just shortterm monitoring of offshore facilities generating wastes but also long term monitoring and surveillance to ensure that operators comply with the provisions of EGASPIN.

Consequently, the government should ensure that DPR is provided with funding, state-of the-art equipment and trained personnel to enable it to carry out its monitoring and inspection functions.

The Nigerian government must shun its lackadaisical attitude and be more proactive in the enactment and amendment of oil and gas laws.

3.0 References

Adesina T.O. (2014): *Control of oil Pollution and the Assessment of Its Legal Framework*: A B.Sc A Project, Faculty of Law, University of Lagos

Anyanwu J.O. (2014): *Electrochemical processes in marine corrosion and ways of preventing corrosion in the Marine Environment*: an unpublished research work, department of Maritime Management, FUTO Owerri.

Funtana, M and N. Greene (1967): *Corrosion Engineering*, "McGraw, New York.

Gadag R.V. & Nityananda A. (2010): *Engineering Chemistry.* International Pvt Ltd, 30 Sep 2010 - 356 pages

Hougen, O.A, K.M. Watson and R.A Raatz, " *Chemical Process Principles*" part 11, p.1034 New York 1959

Jerry M. Neff, (2008). 'Estimation of Bioavailability of Metals from Drilling Mud Barite', 4/2 Integrated Environmental Assessment and Management 184

Kadafa, A.A.; Zakaria, M.P.; Othman, F. Oil Spillage and Pollution in Nigeria: Organizational Management and Institutional Framework. *Journal of Environ. Earth Sci.* 2012, 2, 22– 30.

Lee, R., R. Seright, M. Hightower, A. Sattler, M. Cather, B. McPherson, L. Wrotenbery, D. Martins, and M. Whitworth. (2002). "Strategies for Produced Water Handling in New Mexico": Ground Water Protection Council Produced Water Conferences, Colorado Springs, pp.16 – 17. http://www.gwpc.org/meetings/PW2002/Papers-Abstracts.htm.

Olukayode A.A. (2015): *Assessment of oil spillage and its control in the oil and gas industry in Nigeria*. Thesis project, postgraduate studies, Ahmadu Bello University, Zaria

Onyema, H.K.; Iwuanyanwu, J.O. Emeghara G.C. (2015): Evaluation of Some Physicochemical Properties and Heavy Metals in Post-Treated Produced Water from Offshore Locations in the Niger Delta Area, Nigeria. *Journal. Appl. Sci. Environ. Manage. Dec., 2015. Vol. 19 (4)767-770. JASEM ISSN 1119-8362*

Onwuegbuchunam, D.E, Ebe, T.E, Okoroji, L.I. and Essien, A.E. (2017): An Analysis of Ship-Source Marine Pollution in Nigeria Seaports. *Journal of Marine Science and Engineering.* J. Mar. Sci. Eng. **2017**, 5, 39; doi:10.3390/jmse5030039. www.mdpi.com/journal/jmse

OECD, 1997. *Organisation for Economic Co-Operation and Development, The Environmental Effects Of Freight*. Paris: Head of Publications Service.

Olof & Jonas (2015): *Oil Contamination in Ogonil and, Niger Delta*: the Royal Sweden Academy of Sciences

Osuji N.J. (2015): *An appraisal of management of oil pollution from maritime activities in the Nigerian coastal waters*. unpublished m.sc thesis. federal university of technology, Owerri.

Telleza, G.T.; Nirmalakhandan, N.; Gardea-Torresdey, J.L. (2002)Performance Evaluation of an Activated Sludge System for Removing Petroleum Hydrocarbons from Oilfield Produced Water. *Advanced Environment. Resource. 2002,* 6,455–470.

Wesley, D and Fowler, S.A. *Marine Metal Corrosion* A Layman's Guide to Corrosion Associated With Pleasure Craft Metals

Veil J. A. and Clark C.E. (2010). Produced Water Estimates and Management Practices. SPE 125999, Presented at the International Conference on Health, Safety and Environment in Oil and Gas Exploration and Production, Rio de Janeiro, 12-14 April.