PHYSICO-CHEMICAL ANALYSES AND CORROSION EFFECT OF PRODUCED WATER ON LOW CARBON STEEL

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ABSTRACT

The corrosion effect of produced water on low carbon has been investigated using the weight loss technique. The composite produced water sample was found to contain pH (5.3), turbidity (82 NTU), conductivity (8920 Ns/cm), salinity (2394 mg/L), total iron (1.28 mg/L), carbonate (140 mg/L), nitrate (42.74 mg/L) and suphate (nil mg/L). At an exposure time in hours of 120, 240, 360, 480, 600, and 720, the corresponding calculated corrosion rates in many of the coupons were 0.077, 0.153, 0.204, 0.345, 0.352, and 0.370 respectively. Physico-chemical characteristics of the composite produced water sample used for the study has a higher concentration compared with DPR standard for discharge of produced formation water into surface environment. It was assumed that the corrosion of the coupons was due to presence of high chemical matters in the produced water sample.

KEY WORDS: Corrosion, produced water, environment, rock, salinity, dissolved oxygen.

INTRODUCTION

The production and export of oil and gas play a dominant role in Nigeria's economy and account for about 90 percent of her gross earnings (Okoko and Nna, 1998). The improvement and sustenance of this key sector of the nation's economy led to the discovery and investment in new oil fields.

Produced water is generated at the drilling and production phases of a well. It is an extricable part of hydrocarbon recovery process. It accompanies crude oil and gas from drilling well.

Produced water is mostly composed of reservoir fluids, dissolved and suspended solids, metallic salts and heavy metals. In some instances, produced water could leach radioactive elements from geological formations and transported to the surface (Khatib and Verbeek, 2002).

Produced water, if discharged into environment can have negative effects. This could in the long-term lead to adverse impact on soils, surface and ground water in the discharge area (Ashim, 1998). Salt water accompanying oil production is a potential source of pollution in the petroleum industry and hence the management of produced water is a challenge for mature fields and for the development of remote fields (Barley, 2000). Although, the physico-chemical characteristics of produced water may vary from one formation to another, its properties has been reported to be responsible for failure of most drilling operations (Nelson, 1985).

Water samples that tend to corrode metals or materials that are in contact with it are termed corrosive. Corrosiveness is a measure of corrosion damage at specific concentrations of the corrosion agents in water (Jones, 1988). Blake (1980) ascertained that water can be corrosive if it has (i) a low pH value (high acidity), (ii) high free carbon dioxide, and (iii) absence of temporary hardness (low alkalinity). Corrosive properties of produced water form the basis for this study. This paper presents a study on the corrosive tendencies of produced water by carrying out an intensive chemical analysis and corrosive aggressiveness of sampled produced water.

MATERIALS AND METHODS

Produced water samples used for the study were collected during the drilling campaign in Azuzuama field, within the month of October 2003. Azuzuama field is located in Southern Ijaw Local Government Area of Bayelsa State. It is within the coordinates of 10500 - 16700E and 150000 - 325000N in the lower plains of the lower Niger Delta of Nigeria.

Produced water was collected at a depth interval of 500m starting at a depth of 2000m till 3500m. At the required depth of 2000m, 2500m, 3000m and 3500m produced water samples were collected in one (1) litre plastic containers. The plastic containers were pre-treated by washing each with dilute Hydrochloric acid and dried (DPR, 2002). At the collection point and depth, each plastic container was rinsed twice with relevant samples and filled to the rim. Samples were identified by labels on the containers.

Produced water samples were analysed for the following physico-chemial properties: pH, turbidity, salinity, total dissolved solids (TDS), dissolved oxygen (DO), electrical conductivity, total iron, carbonate, nitrate and sulphate. These parameters were chosen because they were good environmental indicators for corrosion risk assessment (DPR, 2002). The pH, turbidity, salinity, total dissolved solids, dissolved oxygen and electrical conductivity was determined using multi-parameter water quality monitor. At the determination of any of these parameters, the instrument was properly checked and calibrated before and after use. Nitrate, carbonate and sulphate were determined using Brucine colourimeter technique. Total iron content of the samples was determined using Atomic Absorption spectrophotometer (AAS) Perkin-Elmer Model 3110. All methods of analyses were consistent with APHA (1990) and DPR (2002).

For the corrosion testing of samples, sheets of low carbon steel (0.1 – 0.2 percent carbon content and density 7.82g/cm3) were obtained from a corrosion company in Port Harcourt. These sheets were cold cut to the dimension 4 x 4 x 1cm. The cold-cut technique was used to maintain the integrity of the steel and hence avoid the probable effect of heat-affected zone (HAZ) on corrosion. Each coupon was perforated with hole of the same diameter at the side to allow the passage of a thread. The average weight of the coupons ranged from 20.000g to 20.224g. Six pieces of coupons were prepared for the study. The coupons were surfaced finished by scrubbing with sand paper, sterilized by dipping in absolute ethanol and degreased by washing in acetone. Coupons were dried in an oven at a temperature of $60^{0}C$ for 15 minutes. They were allowed to cool over night in a desiccator. The methods of coupons preparation were as reported (Avwiri and Tay, 1999).

Produced water sample used for corrosion testing was formed by bulking produced water samples collected at the various depths. Physico-chemical characteristics of the bulked produced water were also determined. The coupons were immersed in a beaker containing the water sample. Pre-

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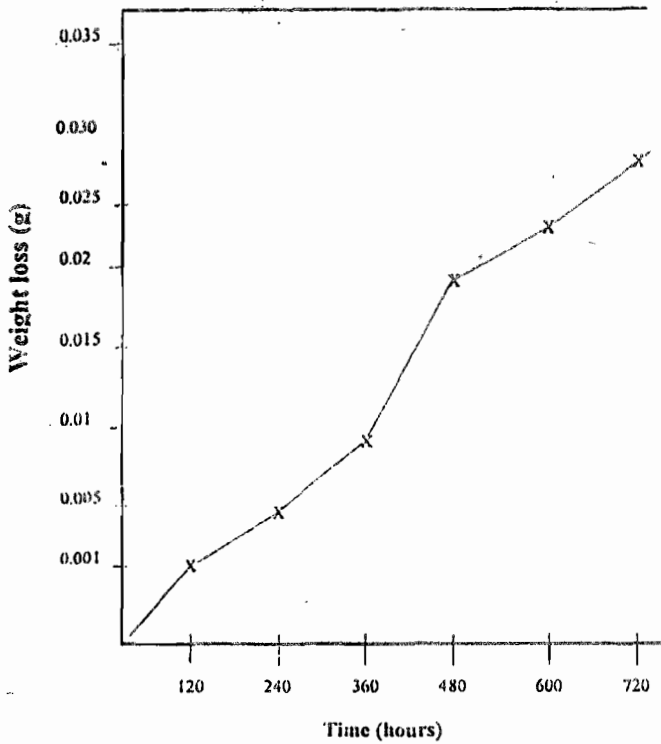
Figure 1: Variation of weight - loss with exposure time
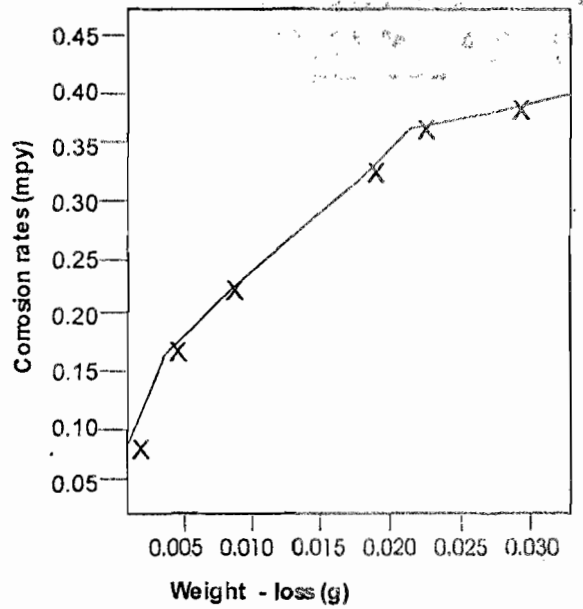

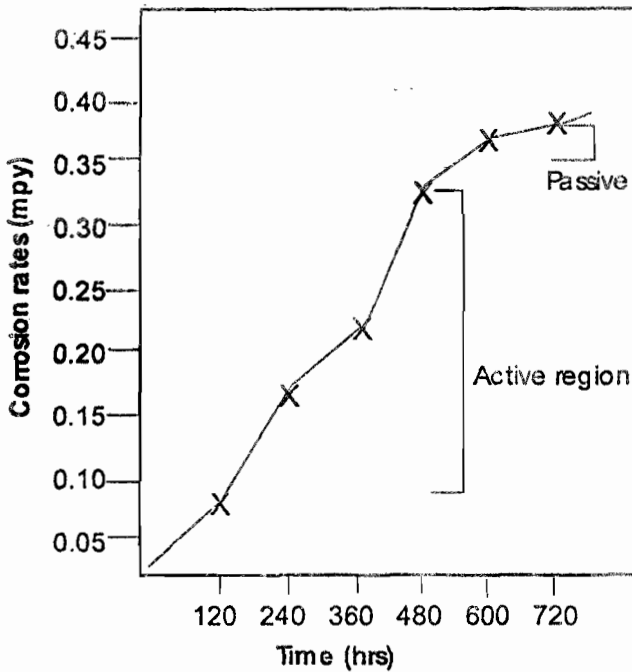Figure 3: Variation of corrosion rates with weight-loss for corrosion

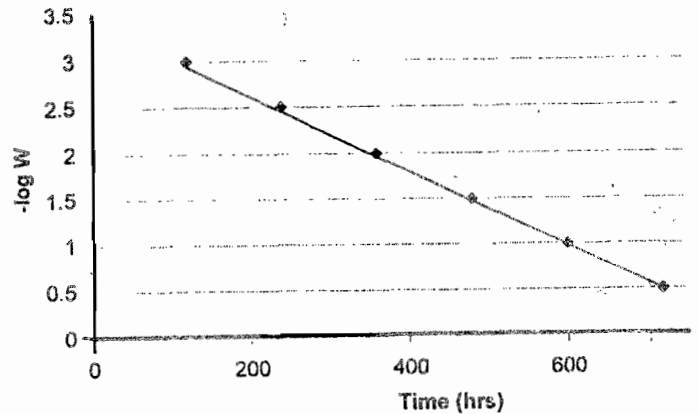Figure 2: Variation of corrosion rates with exposure time

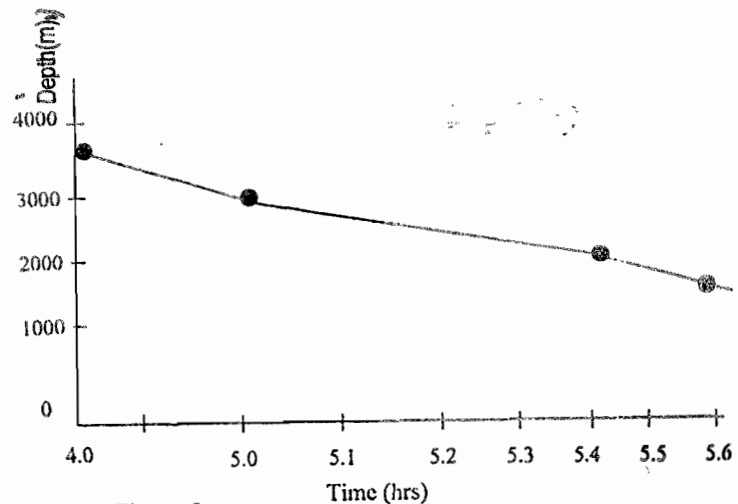Figure 4: Plot of log W versus Time

Figure 5:
Variation of pH of produced water samples with depth.

weighed coupons were immersed in the test solution for 30 days. A coupon was withdrawn ever 5 days for re-weighing. Corrosion rates were determined using the conventional weight-loss method (Bradford, 1993), as stated in equation 1.1

$$R = \frac{kw}{ATD} \quad \text{.............. 1.1}$$

Where:

R = Corrosion rate in mils per year (mpy)
W = Weight loss in grams
A = Original surface area of coupons (cm^2)
T = Exposure time (hours)
D = Density of coupons (g/cm^2)

K = Constant (3.45 x 10°)

$$W = W_o - W_f \quad \text{.............................. 1.2}$$

Where;

W_o = original weight of coupon before testing
W_f = Weight of coupon after testing

$$A = 2 (LW + LH + WH) \quad \text{............................. 1.3}$$

L = Length of the coupon
H = Height of the coupon

Table 1: Physico-Chemical Characteristics of Produced Water Sample

Parameters / Units	Sample concentration at various depths				Composite sample	DPR Limits for produced water discharge
	2000m	2500m	3000m	3500m		
PH	5.6	5.4	5.0	4.9	5.3	6.5-8.5
Turbidity (UTU)	84	80	70	76	82	< 15
Cond. (NS/cm)	7800	9000	9020	9100	8920	-
Salinity as Chloride (mg/L)	2343	2360	2407	2513	2394	600
Total dissolved Solids (mg/L)	8494	8498	8502	8509	8501	2000
Dissolved oxygen (mg/L)						
Total Dissolved solids (mg/L)	1.02	1.26	1.34	1.39	1.28	1.0
Carbonate (mg/L)	186	175	160	140	180	200
Nitrate (mg/L)	42.68	42.69	43.10	43.35	42.74	10
Sulphate (mg/L)	Nil	Nil	Nil	Nil	Nil	10

Table 2:Corrosion rates for low carbon steel in composite produced water sample

Wo(g)	Wf(g)	W=Wo – Wf	Exposure time (Hrs)	Corrosion rate (mpy)
20.034	20.033	0.001	120	0.077
20.178	20.174	0.004	240	0.153
20.001	19.993	0.008	360	0.204
20.000	19.982	0.018	480	0.345
20.224	20.201	0.023	600	0.352
20.000	19.971	0.029	720	0.370

Figure 6:

Variation of carbonate concentration water of produced water samples with depth samples.

RESULTS AND DISCUSSION

Results of the physico-chemical analyses of produced water samples and corrosion testing of the composted produced water samples are presented in Tables 1 and 2 respectively.

Figures 1-3 illustrate the plots of weight-loss relationship with time, corrosion rates with time, and corrosion rates with weight-loss respectively.

From the obtained results, the pH values range from 4.9 to 5.6 of the water samples and depict an acidic medium. Bradford (1993) suggested that acidic environment with pH < 6 are more corrosive than pH from 6-8 or alkaline pH<8. The acidity of the water sample may have resulted from corrosive gas such as carbon dioxide, that have entered the system through chemical decomposition of calcium carbonate and which was converted into carbonic acid (Stott and Herbert, 1986).

The carbonate (CO_3) concentrations for the water samples were low (140-186 mg/l) and that for sulphate (SO_4) was nil. The low concentration of CO_3 and nil concentration of SO_4 could have resulted from scale precipitation down hole. Scales are deposits that precipitate directly from water in petroleum production operations. Scales commonly encountered in oil and gas production operations are calcium suphate, Barium sulphate, calcium carbonate and strontium suphate (Jones, 1988).

The nitrate and total iron concentrations ranged 42.68 – 43.35 mg/l and 1.02 – 1.39 mg/l respectively. The iron content of the water samples indicates the problem of iron oxidation. This is further collaborated with the high level of dissolved oxygen (5.3-6.4mg/l) present in the water samples.

The high concentration of salinity that was measured as chloride concentration (2343-2513mg/l) could have been created by the contact of the water sample with the minerals present in the rock.

Figure 1 shows the graphical relationship between weight-loss in grammes and time in hours. The graph indicates the relationship between the two variables. This relationship is given mathematically (Uhlig, 1948), as
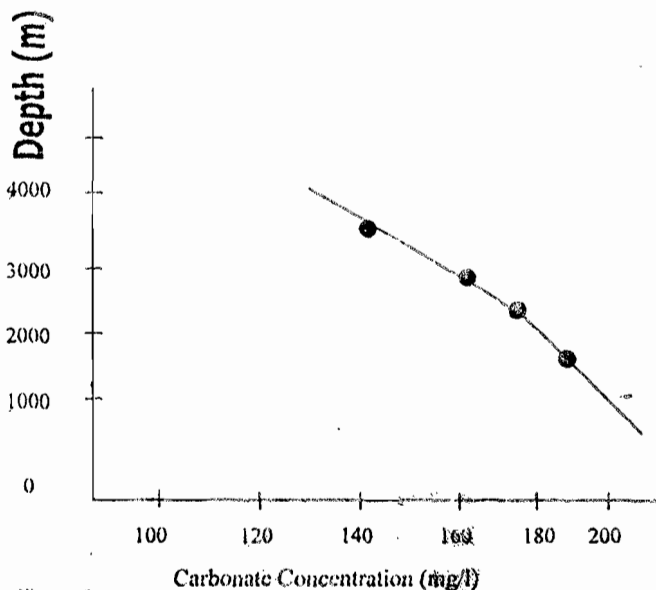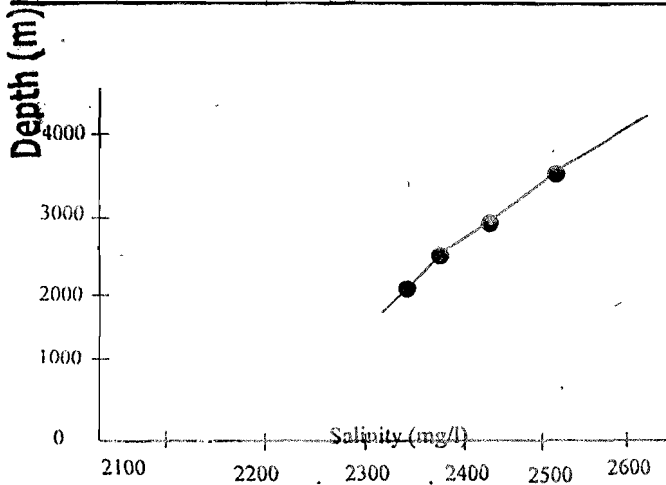
Fig. 7: Variation of salinity of produced water samples with depth

Figures 8:   Conductivity (µS/cm)

Variation of conductivity of produced water samples with depth.

Figure 9: Variation of turbidity of produced water samples with depth

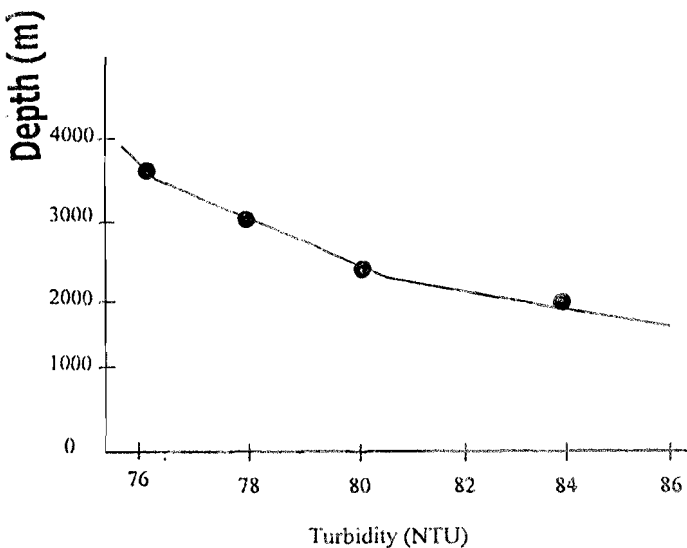$$W_L = K_B t \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots 1.4$$

Where W_L is weight-loss in grammes and it is the time of exposure in hours and K_B is the proportionality constant which depends upon the factors contributing to the behaviour

Figure 10:   Variation of iron concentration of produced water samples with depth.

of steel in a specific environment. From Figure 1., K_B is approximately 4.67 x 10^{-5}, indicating he nature of the corrosive environment. The figure shows the influence of produced water on the corrosion of low carbon steel. The corrosion is attributed to the presence of corrosive elements especially hydrogen ions which accelerate the corrosion process. The corrosive action on the low carbon steel suggests a high degree of aggressiveness of the produced water. This is consistent with previous report for steel in acidic environment (Ovri, 1998).

Figure 2 shows the relationship between corrosion rates and exposure time up to 480hrs. However, it was observed that the corrosion rate was beginning to slow down from 600 hours. This illustrates the typical behaviour of a metal that demonstrates passivity effects. The behaviour of the low carbon steel can be conveniently divided into two regions, active and passive. In the active region, the behaviour of this material is identical to that of a normal metal. From 480 hours, the passive region begins. The decrease in corrosion rates could be attributed to the formation of a surface film or protective film. The passivity displayed is due to the formation of protective oxide film on the coupon surface and this lowers corrosion rates (Evans, 1968).

A similar observation has been made for metals such as iron, nickel, silicon, chromium, titanium and alloys containing these metals (Bradford, 1993).

Figure 3 illustrates the relationship between corrosion rates and weight loss. It indicates a general increase in weight loss with increase corrosion rates. This increase corresponds with the general rule guiding chemical reactions (Sherwood, 1971).

When log W was plotted against time (Figure 4) a linear variation was observed which confirms a first order reaction kinetics with respect to low carbon steel in produced water.

The plots for the variations of produced water samples collected at various depths against pH, carbonate, salinity, conductivity, turbidity, and total iron concentrations are presented in Figures 5-10 respectively. Figure 5 reveals that produced water becomes more acidic (decreasing pH values) with increasing depth. This agrees with previous report for corrosive environment (Ovri, 1998). Figure 6 illustrates the relationship between carbonate concentrations of produced water samples with increasing depth down hole. Carbonate concentration decreases with increasing depth. Figure 7 shows the graphical relationship between salinity concentrations of produced water sample with increasing

depth. The graph indicates a linear relationship between the variables. That is, as the depth increases salinity increases. Figure 8 illustrates the relationship of conductivity of produced water samples with increasing depth. As the depth increases conductivity of samples increases. Figure 9 is graphical relationship between turbidity of produced water samples with increasing depth. From the Figure 9 turbidity decreases with increasing depth. Figure 10 is an illustration of the relationship between the concentrations of iron in the produced water samples with depth. Figure 10 shows a corresponding increase in iron content of produced water samples with increase in depth.

CONCLUSION

The study shows that produced water samples collected from Azuzuama field are acidic (average pH of 5.3). Also, the corrosion rates of carbon steel were enhanced by the phenomenon of produced water. It is therefore recommended that produced water be treated and disposed in accordance with regulatory requirements and best practices.

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