Estimation of Microbiologically Influenced Corrosion of X60 Steel Exposed to a Natural Freshwater Environment

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Abstract
The effects of microbial activities on the corrosion of X60 steel exposed to a natural freshwater environment (Orashi River) have been experimental determined. In the petroleum industry in Nigeria, construction material for pipeline is made of X60 steel and such pipeline traverses a number of natural freshwater environments. Outcome of this investigation provides opportunities for examining the possible effect of microorganisms on the corrosion of X60 steel. Physicochemical and biological characteristics of water samples show the levels of measured parameters that favours the promotion and sustenance of microbiologically influenced corrosion. Total bacterial population varied from $10^3$ cfu/ml to $10^6$ cfu/ml in all water samples indicating a population that can initiate microbial corrosion. Corrosion rate was calculated to be 0.79 mpy after 6920 hours of test period. An approximate linear relationship between mass loss and time for the first 5376 hours was obtained. An approximate sinusoidal behavior for log of mass loss with time suggested a second order chemical reaction between the microorganisms and the metal. The presence of biofilms on the surface of the X60 steel accounts for the observed reactions. Biofilm formation on the surface of the coupons followed the four phases of biofilm evolution biomass amount per carrier for the period of the test. In all these phase, biomass accumulation increased with time. The superficial biomass formed on the metal surfaces increased with time during the experimental period.

Keywords: microbiologically influenced corrosion, X60 steel, Orashi River, biofilms, corrosion rate.

INTRODUCTION
API X60 steel is commonly and frequently used for pipeline works in Nigeria’s oil and gas industry. Although X60 steel is susceptible to corrosion, its wide application in pipeline construction and above ground storage tanks (AGST) is based on its low cost, high strength and ease of field make-up by welding. Elemental composition of X60 steel is presented in Table 1.

Table 1: Elemental composition of X60 steel (Benmoussat and Hadjel, 2005)

<table>
<thead>
<tr>
<th>C (%)</th>
<th>Mn (%)</th>
<th>P (%)</th>
<th>S (%)</th>
<th>Cr (%)</th>
<th>Ni (%)</th>
<th>Mo (%)</th>
<th>V (%)</th>
<th>Cu (%)</th>
<th>Al (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.199</td>
<td>1.59</td>
<td>0.016</td>
<td>0.018</td>
<td>0.015</td>
<td>0.007</td>
<td>0.008</td>
<td>0.004</td>
<td>0.024</td>
<td>0.024</td>
</tr>
</tbody>
</table>

The influence of microorganisms on the corrosion rate of metals in various systems such as underground pipelines, cooling water systems, drilling operations, marine structures and waste water treatment facilities have been reported (Harris, 1960; Videla, 1996; Mittelman, 2003 and Iversen, 2001). It is estimated that about 20 percent of all corrosion damage of metals are microbiologically influenced or enhanced (Booth, 1971). Damages resulting from microbial corrosion in production, transport, and oil storage facilities amount to hundreds of millions US dollars per year in United States of America (Costerton and Boivin, 1991).

One of the keys to the alteration of conditions at a metal surface, and hence the acceleration or delay of corrosion, is the formation of the biofilm. Biofilms affect the interaction between metal surfaces and the environment, not only in bio-deterioration processes such as corrosion, but also in several biological processes applied to materials recovery and handling. In principle, microbiologically influenced corrosion is an interfacial process. The kinetics of microbiologically influenced corrosion is determined by the physico-chemical characteristics of the environment at the interface between the metal surface and microorganisms at the surface. Such physico-chemical parameters include concentration of oxygen, salts, pH value, redox potential and conductivity, which can be influenced by microorganisms growing at the surface of a metal.
Microbiologically influenced corrosion is a biofilm problem as the microbial influence is due to layers of microorganisms in contact to the interface where the corrosion process takes place. Thus, reliable, and representative information about biofilms is mandatory for a better understanding of microbial corrosion (Pritchard, 2002). However, the actual role of biofilm in microbiologically influenced corrosion process is still a strong academic exercise (Picoureaux and van Loosdrecht, 2002). This work examines the role or influence of biofilm on the corrosion of API X60 steel in a natural freshwater environment.

MATERIALS AND METHODS

Study Water Body
The freshwater body is Orashi River. The River is a tributary of River Niger. It is a non-tidal freshwater ecosystem. Orashi River flows southwards with a velocity that ranges between 0.5m/s and 1.2m/s depending on the seasonal conditions. The total length of the River is estimated to be 31.7km (NNDC, 2003). The depth and width of the River is also estimated to be between 1.7 and 2.1m and between 17m and 25m respectively (NNDC, 2003). In terms of oil and gas activities, Orashi River traverses the Ogbogene, Obiafu, and Mbede Fields. The oil fields are in Nigerian Oil Mining Leases (OML) 60 with a number of oil and gas facilities such as; Ebocha oil centre, Mbede flow station, Obiafu-Obrikom Gas Recycling Plant, oil wells and flow lines.

Study Site
The study site is a location along Orashi River by Oil well 8 location (Northing 249620 and Easting 416240). The choice of this site was based on the following: vicinity of industrial/oil and gas activities, flow region of speed between 0.8 and 1.12m/s, and presence of humic substances. These characteristics are consistent with those identified for assessing microbiologically influenced corrosion hazard (Stein, 1995).

Determination of the Physico-Chemical and Biological Characteristics of the Water Body
At the study site, water sample was collected using plastic containers pre-treated by washing them with 0.1M dilute hydrochloric acid and sun-dried. At the sample collection point, the plastic containers were first of all rinsed with the water to be collected. One container at a time, with its lid closed was then dipped into the water body to a depth of about 1.0m and the lid removed to fill the container with water. The lid was replaced immediately, and the container with the water sample taken out of the water body. (Replacing the lid of the container at the sampled depth excludes air and prevents contamination of the water sample with microorganisms from the environment). Samples for microbial analysis were collected in sterilized McCartney glass bottles and stored in an ice-chest. Water sample were transported immediately to the BGI laboratory, Port Harcourt for analysis. Note, that at every time of sample collection, a record was kept on the sample container indicating date, and time. Sample was properly handled and all necessary quality assurance and quality control (QA/QC) measures such as preservation, storage, and labeling, were taken.

Water sample was collected five times throughout the study period of 10 months (June, 2010 – March, 2011), with at intervals of 2 months (i.e. 2, 4, 6, 8 and 10 months).

At the field and the laboratory samples were analysed for the following parameters; pH, temperature, turbidity, redox potential, electrical conductivity, total organic carbon (TOC), dissolved oxygen (DO), total dissolved solids (TDS), nitrate, sulphate, and total microbial count (TMC). These parameters are good environmental impact indicators for microbiologically influenced corrosion assessment (Videla, 1996; Stein, 1995). pH, temperature, turbidity, electrical conductivity, dissolved oxygen (DO), total dissolved oxygen (TDS), was measured in-situ using a multi-parameter water quality (model 600 UPG). Note that the multi-parameter water quality monitor was properly checked and calibrated before and after use. Redox potential was measured in-situ using Orion multimeter (model 1260) and combined platinum / silver (silver chloride electrodes). The amount of sulphate in the samples was determined using turbidimetric method. Nitrate concentration of samples was determined using the Ultraviolet Spectrophotometric screening technique (Unicam uv/visible spectrophotometer-MS/27), (APHA, 1992). Total organic carbon of samples was determined using an automated TOC analyzer (ESML 690). Total microbial count of samples was determined using the rapid agar dipstick method. The choice of the rapid agar dipstick method is based on its ease of application and reliability; it can be used on site and is widely reported in literature (Bloomfield et al., 1998; Wang et al., 2006). Into each sample, an agar nutrient dipstick was dipped into it for 20 minutes. The stick was then retrieved from the system and incubated in a warm oven for 24 hours. The population of microorganisms was determined by comparing it with a calibrated chart provided by the manufactures (Boots Micro – check company, Nottingham, UK). All methods of analyses applied in this study are consistent to that of the Department of Petroleum Resources (DPR, 2002), American Public Health Association (APHA, 1992).

Preparation of Corrosion Coupons
Sheets of X60 steel (0.1-0.2 percent carbon content, and density of 7.82g/cm³ were obtained from a
Tricorr Technology Company, Port-Harcourt and cold-cut into smaller sheets 10cm long, 5cm wide, and 0.5cm thick (i.e. 10cm x 5cm x 0.5cm). The cold-cut technique was used to maintain the integrity of the steel and hence avoid the probable effects of heat-affected zone (HAZ) on corrosion. Each coupon was perforated with a hole of the same diameter at the side to allow the passage of a thread. The coupons were surface-finished by scrubbing with sand paper and sterilized by dipping in absolute ethanol and degreased by washing in acetone. The coupons were then dried in an oven at a temperature of 60°C for 15 minutes, and were cooled over night in a dessicator. The average mass of a prepared coupon ranges from 19.75 to 19.97g, and 5 (five) pieces of corrosion coupons were prepared for the study. The method used in preparing the coupons is consistent with known methods (Awviri and Tay, 1999). The prepared coupons were weighed before and after each test using a weighing balance (Mettler Balance Model AE 166) with the mass of each coupon determined to the nearest 0.001g.

Experimental Procedure
At the study site by the bank of Orashi River, the prepared coupons were suspended into the water body at different points. The coupons were suspended in the water body with the aid of strings attached to an external anchor. The coupons were left in the water environment for a period of 10 months with a temperature of 60°C, at intervals (hours). The acidic pH may have resulted from substances such as oxides of sulphur, nitrogen and carbon that have entered the atmosphere via gas flaring (a common feature in the study area) which are converted to sulphuric acid, nitric acid and carbonic acid, after rainfall which has been similarly observed (Rim et al., 2005). The pH values of the water samples is within the range 4 to 9 identified by Costerton et al., (1995) to be suitable for bacteria growth.

The temperature of the water samples range from 26.7°C to 28.7°C. This temperature is suitable for bacteria growth (optimal temperature for bacteria growth lies between 25°C and 30°C (Booth, 1971). Electrical conductivity of the water samples ranges from 132μs/cm to 149μs/cm, indicating the presence of ions in the water bodies. These high electrical conductivity values may have resulted from seawater intrusion, as observed for Warri River sample collected at Warri Refinery and Petrochemical Company (WRPC), Effurun (Egborge, 1994).

$\Delta M = \frac{\Delta M \times 3.45 \times 10^6}{A \rho t}$

where $\Delta M$ is the mass loss (g) of the coupon, $A$ is the total exposed surface area of the coupon (cm$^2$), $\rho$ is the density of the coupon (g/cm$^3$), and $t$ is time (hours).

The mass loss and total surface area of coupon are calculated as

$M = M_o - M_f$

$2.0 A_o = 2(LW + LH + WH)$

where, $M_o$ = Initial Mass of coupon before testing; $M_f$ = Final weight of coupon after testing; $L$ = Length of the coupon; $H$ = Thickness of the coupon; $W$ = Width of the coupon.

RESULTS AND DISCUSSION

Physico-Chemical and Biological Characteristics of the Water Body

Results of the physico-chemical and biological analyses of water samples collected from Orashi River by oil well 8 (study site) are presented in Table 2.

Table 2: Physico-chemical and biological characteristics of the water body

<table>
<thead>
<tr>
<th>Parameters/Units</th>
<th>Sampling Period (Months)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>2</td>
</tr>
<tr>
<td>pH</td>
<td>6.6</td>
</tr>
<tr>
<td>Temp. (°C)</td>
<td>28.7</td>
</tr>
<tr>
<td>EC (µS/cm)</td>
<td>136</td>
</tr>
<tr>
<td>Turb (NTU)</td>
<td>18</td>
</tr>
<tr>
<td>Redox Potential</td>
<td>-107</td>
</tr>
<tr>
<td>TOC (mg/l)</td>
<td>15.3</td>
</tr>
<tr>
<td>TDS (mg/l)</td>
<td>1917</td>
</tr>
<tr>
<td>DO (mg/l)</td>
<td>4.1</td>
</tr>
<tr>
<td>NO$_3$ (mg/l)</td>
<td>6.7</td>
</tr>
<tr>
<td>SO$_4^2-$ (mg/l)</td>
<td>0.8</td>
</tr>
<tr>
<td>TMC (cfu/ml)</td>
<td>10$^5$</td>
</tr>
</tbody>
</table>

Source: Experimental, 2010/2011
Turbidity values of all water samples lie within the range 18NTU-31NTU. The relatively high values of turbidity for all samples may be the result of both suspended and dissolved solids in the water such as silt, finely divided organic and inorganic matters, and soluble coloured organic compounds. Also, erosion of sediments from the bank of the water body and runoff may have contributed to the observed levels of turbidity. These materials are potential sources of organic carbon which is utilized by bacteria for the production and development of new cellular materials. High level of turbidity promotes growth of microorganisms within an ecosystem (Characklis, 1981). Redox potential (Eh) of all water samples lie within the range -132mV to -107mV. Spectrum of redox potential under which microbial life can be found ranges from -450mV to +850mV, where the negative side of the spectrum favours methanogenic bacteria, and the positive side corresponds to iron bacteria (Newman et al., 1991). However, a negative potential indicates high corrosiveness of that environment (Newman et al., 1991). Thus, the range of negative redox potential value obtained for the samples indicate a corrosive environment.

Variations of TDS and TOC in all water samples analysed has the level of TDS that range from 1908 mg/l to 2571mg/l, while that of TOC lies within the range 11.7mg/l – 17.1mg/l. Carbon is the most abundant cell constituent, and can be obtained from organic matter (Videla, 1996). The presence of decaying organic matter (leaves) that contributes to TDS and TOC is commonly observed in the area. The water body provides an excellent condition for bacteria growth because of the high levels of TDS and TOC. On the other hand, organic carbon is utilized by bacteria for the production of new cellular material (assimilation) and as an energy source (dissimilation).

Dissolved oxygen in all water samples ranges from 3.9 mg/l to 5.2 mg/l, indicating an environment that promotes growth of aerobic microorganisms. The level of oxygen in an environment plays an important role in corrosion process especially where oxygen reduction is generally the main cathodic reaction.

The concentration of nitrate ions (NO$_3^-$) in all water samples varied from 6.7mg/l to 9.1mg/l, while that of sulphate ions (SO$_4^{2-}$) varied from 0.8mg/l to 1.3mg/l. There must be adequate supply of nutrients for synthesis of new cells and generation of energy in any aquatic environment that sustains bacteria growth. Lack of these elements limits growth and activity of microorganisms, whereas their abundance results in uncontrolled microbial growth. The levels of nitrate could be attributed to the processes of photochemical oxidation of nitrogen to give oxides of nitrogen during lightening and thunderstorms which become soluble during rainfall (Rim-Rukeh, et al, 2005).

Total bacterial population varied from $10^3$ cfu/ml to $10^5$ cfu/ml in all water samples analysed, indicating adequate bacterial population for microbiologically influenced corrosion activity. It has been suggested that Sulphate Reducing Bacteria (SRB) level of $10^4$ cells/cm$^3$ is a clear indication of possible corrosion problem, while a relative population of $10^5$ cells/cm$^3$ of microorganisms is a concern of potential corrosion problem in an environment (Costello, 1969).

**Corrosion Assessment by Mass Loss Method**

Corrosion rates of X60 steel influenced by biofilms formed on the surface of metal in the natural aqueous environment are presented in Table 3.

<table>
<thead>
<tr>
<th>Exposure time (hours)</th>
<th>Mf (g)</th>
<th>Mi (g)</th>
<th>AM (g)</th>
<th>Biomass (mg)</th>
<th>Corrosion Rate (mpy)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>19.79</td>
<td>19.79</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>1344</td>
<td>19.79</td>
<td>20.16</td>
<td>0.37</td>
<td>0.17</td>
<td>1.06</td>
</tr>
<tr>
<td>2688</td>
<td>19.91</td>
<td>20.95</td>
<td>1.04</td>
<td>0.68</td>
<td>1.48</td>
</tr>
<tr>
<td>4032</td>
<td>19.87</td>
<td>21.65</td>
<td>1.78</td>
<td>0.91</td>
<td>1.69</td>
</tr>
<tr>
<td>5376</td>
<td>19.97</td>
<td>21.90</td>
<td>1.93</td>
<td>1.27</td>
<td>1.38</td>
</tr>
<tr>
<td>6720</td>
<td>19.75</td>
<td>21.15</td>
<td>1.40</td>
<td>1.46</td>
<td>0.79</td>
</tr>
</tbody>
</table>

Source: Experimental, 2010/2011

Corrosion rates increased with time for the first 4032 hours of the test and decreased for the remaining part of the test period (Fig. 1.) This illustrates the typical behaviour that demonstrates passivity effects as have been similarly observed (Rim-Rukeh, 2005; Evans, 1968). The behaviour of the X60 steel can be conveniently divided into two regions: active and passive. The decrease in corrosion rates could be attributed to the thickness of biofilm formed on the surface of the metal. Picioreanu et al, 2001 had observed that biofilm have the potential of protecting a metal from corrosion.

![Fig. 1.0: Variation of corrosion rate of coupons with time.](image1.png)

![Fig. 2: Variation of mass loss of coupon with time.](image2.png)
Figure 2 illustrates the mass loss of coupons in the natural environment during the period of the experiment, indicating approximate linear relationship between \( \Delta M \) and \( t \) in the form

\[
\Delta M = kt + C \quad (4.0)
\]

where \( k \) is a proportionality constant that depends on the conditions in a specific environment, and \( C \) is the intercept of the straight line on the vertical axis. Figure 2.0 shows increase in mass loss of the coupons with time for the first 5376 hours. However, at about 6720 hours of the test period the mass loss decrease probably because of the decrease in corrosion occasioned by the level of biofilm formed on the metal surfaces.

When the log of mass-loss is plotted against time, an approximate sinusoidal curve is obtained (Fig. 3), which suggest a second order chemical reaction between the microorganism and the metal. This method of using a sinusoidal relationship between log of mass-loss and time in determining the order of a reaction is not reported in the literature, this aspect of the study requires further investigation.

Figure 4.0 shows the relationship between the superficial biomass formed on the metal surfaces with time during the experimental period. It is very similar to the sigmoidal fashion of biofilm development presented by Bryers and Characklis, 1982 and Picoreau et al, 2001. Four phases can be clearly distinguished in the evolution of biomass amount per carrier for the period of the test. In all these phases, biomass accumulation increased with time, because biomass accumulation is the net result of growth and detachment. This suggested that the rate of biofilm growth is faster than the rate biofilm detachment as has been similarly observed van Loosdrecht et al (1995). Biofilm detachment rate must be slower for biofilm structure formation because it is the primary process that balances growth. The process of detachment result to increase in the availability of substrate for the remaining and hence subsequent biofilm increase.

**CONCLUSION**

Physicochemical and biological characteristics of water samples collected by oil well 8 (study site) along Orashi River have been presented. It is shown that the levels of measured parameters in water samples are consistent with the conditions in an environment that favours microbial activity. The water body, therefore, exhibits the necessary qualities for promotion and sustenance of microbiologically influenced corrosion. It is shown that corrosion coupons made of X60 steel immersed in the natural water environment corroded microbiologically at the rate of 0.79 mpy after 6920 hours of test period.

Mass loss of coupons in the natural environment during the period of the test indicates an approximate linear relationship between mass loss and time for the first 5376 hours. The linearity disappeared after 6720 hours of the test period. The log of mass-loss against time, gave an approximate sinusoidal curve which suggested a second order chemical reaction between the microorganism and the metal.

The superficial biomass formed on the metal surfaces increased with time during the experimental period.

**REFERENCES**


