Comparative Study of Microbial and Non-microbial Corrosion of X60 Steel Exposed to Produced Water

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Abstract: A comparative study of microbial and non-microbial corrosion of X60 steel exposed to produced water is presented. The laboratory investigation involves X60 steel coupons immersed in two batch reactors 1 and 2. Reactor 1 contains produced water with 0.5ppm dissolved ozone added on weekly basis to eliminate the microorganisms naturally present in the water, while reactor 2 contains the same volume of produced water with 2g of artificial fertilizer (NPK 15-15-15) added on weekly basis as nutrient-supplement to promote growth of microorganisms in the produced water. It is shown that the corrosion rate of X60 steel influenced by microorganisms in the produced water is about 94% greater than non-microbial corrosion of the metal. The corrosion induced chemical reaction in both reactors is first-order, and microbial corrosion results in pinhole-size pits on the surfaces of the metal.

Key words: Corrosion; X60 steel; Produced water; Microorganisms; Fertilizer

INTRODUCTION

The extent to which a corrosion process will proceed is determined by a number of factors which may be biotic (living) or abiotic (non-living). The abiotic factors include scratches, abrasion on metal surfaces, and presence of salt and corrosives in the surrounding medium. The biotic factors involve the activities of microorganisms and such a corrosion process is known as microbiologically influenced corrosion (MIC) or biological corrosion (i.e. biocorrosion).[1] MIC may, therefore, be defined as an electrochemical process where microorganisms are able to initiate, facilitate or accelerate corrosion reaction without changing its electrochemical nature.[2] The participation of microorganisms in a corrosion process was ignored in the past,[3] but is now acknowledged and remains the focus of present and future research work.[4] Biocorrosion is reported in many systems such as underground pipelines,[5] water treatment plants,[6] nuclear power industries,[7] and marine structures.[8] It is estimated that about 20 percent of all corrosion damage of metals and building materials are microbiologically influenced and enhanced. For example, damage caused by microbial corrosion in stainless steel heat exchangers within 8 years amounts approximately to 55 million US dollars, and microbial corrosion damage in production, transport, and storage oil facilities amounts to some hundreds million US dollars per year in the United States.[8]

It is well known that exposure of steel or any kind of metal in natural water induces the development of microbial film called biofilm. Biofilms are thin distributed films formed by microorganisms such as bacteria, algae and fungi and their associated exopolymers, on the surface of metals. The presence of biofilm on a metal surface often leads to highly localized changes in the concentration of the electrolyte constituents, pH, and oxygen levels.[9] The metabolic processes of the microorganisms are sustained by chemical reactions energized by nutrients obtained from the surrounding environment. These processes can influence the corrosion behaviour of materials by introducing or enhancing local chemical changes at the surface of the metal and producing a localized acid environment. Such conditions produce corrosive deposits and alter anodic and cathodic reactions, depending on the environment and organisms involved. The deposits often stimulate the development of localized form of corrosion such as pitting.[10] Although X60 steel is susceptible to corrosion, it is the material for construction of most pipes used in the oil sector in Nigeria due to its low cost, high strength, and ease of field make-up by welding.
Produced water (or formation water) is one that accompanies crude oil and gas from a producing well. It is an integral component of hydrocarbon recovery process and is usually produced during drilling and production phases of a well. Naturally, the crude oil and produced water contain various microorganisms which must be removed to avoid microbial corrosion of internal surfaces of pipes conveying these materials before/after separating the oil from the produced water and gas. The produced water obtained from the separation process is treated to eliminate microorganisms before discharging into the receiving water body.

A particular difficulty in the assessment and control of microbial corrosion is the inability to distinguish between corrosion caused by microorganisms and that caused by non-microorganisms. This point was emphasized by Geiser and Lewandowski[11] and Pryfogle[12] who suggested that corroded materials should be physically inspected for mosaic deposits on the metal surfaces as a means of distinguishing microbial corrosion from non-microbial corrosion. This paper presents a comparative study of microbial and non-microbial corrosion of X60 steel pipe exposed to produced water during production of crude oil from a producing well and/or during separation of the oil from water and gas.

**MATERIALS AND METHOD**

**Materials:** The materials used in the study are 0.5ppm dissolved ozone, NPK 15-15-15 fertilizer, X60 steel coupons, two (2) batch reactors, and produced water. The inorganic fertilizer (NPK-15-15-15) was manufactured by NAFCON (National Fertilizer Company of Nigeria) in 1999 and contains 0.15g of nitrogen, 0.065g of phosphorus, and 0.125g of potassium. X60 steel presents a microstructure of ferrite and Table 1 shows the elemental composition of the metal.

Ozone is a bluish gas with a characteristic pungent odour. It is an oxidizing biocide that is partially soluble in water and highly unstable as it readily reverts to oxygen. The solubility of ozone in water is related to the amount of ozone in the carrier gas stream. Thus, it is important to produce a gas stream containing a relatively high amount of ozone. For example, the maximum solubilities at 25°C for gas stream containing 1% and 3% ozone are 2.7 and 8.1 ppm respectively. These maximum levels are not obtained in practice because of out-gassing of the carrier gas which removes some of the dissolved ozone. Solubility of ozone also decreases with increasing temperature. Ozone degrades with pH, being fairly stable under certain conditions at pH of 6, and stable at pH of 10. The 0.5ppm dissolved ozone used in the study was prepared by NEK Technical, Port Harcourt, Nigeria. The produced water used in the study contains four groups of microorganisms:[13] (i) Hydrocarbon Utilizing Bacteria (HUB) such as *Pseudomonas* sp. and *Bacillus* sp.; (ii) Heterotrophic Bacteria (HB) such as *Pseudomonas* sp., *Bacillus* sp. and *Norcardia* sp.; (iii) Hydrocarbon Utilizing Fungi (HUF) such *Saccharomyces* sp., *Penicillium* sp., and *Candida* sp.; and (iv) Heterotrophic Fungi (HF) such as *Saccharomyces* sp., *Penicillium* sp. and *Candida* sp.

Table 2 shows some measured parameters of the produced water, where the average value of each parameter was calculated from a set of five experimental readings.

**Preparation of X60 Steel Coupons:** Sheets of X60 steel were obtained from Tricorr (Nig) Ltd., Port Harcourt, Nigeria, and cold-cut to the dimensions 10cm x 5cm x 0.5cm for each coupon. The cold-cut technique was used in order to maintain the integrity of the steel and avoid probable effect of heat-affected zone (HAZ) on the corrosion process of the metal. The coupons were surface-finished by scrubbing with 80 grit sand-papers, sterilized by dipping in pure ethanol, and degreased by washing them in acetone. The exposed surface area of each coupon is 115cm² and is calculated as $2(L_w + L_h + h_w)$ where $L = 10cm$ is the length of each rectangular coupon, $w = 5cm$ is the width, and $h = 0.5cm$ is the thickness (or height) of the coupon. Ten (10) pieces of X60 steel coupons were prepared for the study, and the mass of each coupon ranges from 19.95 to 20.03g.

**Experimental Method:** Twenty (20) litres of produced water obtained from a flow station in Rivers State, Nigeria, was divided equally into two batch reactors 1 and 2. Ten millilitres (10ml) of 0.5ppm dissolved ozone (a biocide) was added to batch reactor 1 to eliminate the microorganisms naturally present in the produced water. The choice of dissolved ozone as biocide is a result of its reported biocidal efficacy on a broad spectrum of microorganisms.[16,17] Two grammes (2g) of NPK 15-15-15 fertilizer was added to batch reactor 2 to serve as source of nutrients for the microorganisms in the produced water. The use of the fertilizer as nutrient-supplement for microorganisms in the produced water is due to its reported efficiency.[14] Five (5) prepared X60 steel coupons were completely immersed in each batch reactor and the experimental set-up was left for a test period of 2016 hours. To ensure that living microorganism does not exist in batch reactor 1 throughout the test period, 10ml of 0.5ppm dissolved ozone was added to this reactor on weekly basis. Accordingly, 2g of the fertilizer was...
Table 1: Elemental composition of X60 steel (\(^{13}\))

<table>
<thead>
<tr>
<th>Element</th>
<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>
<th>Fe</th>
</tr>
</thead>
<tbody>
<tr>
<td>Value</td>
<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>
<td>98.095</td>
</tr>
</tbody>
</table>

Table 2: Some measured parameters of produced water used in the study

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Average value</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>5.7</td>
</tr>
<tr>
<td>Turbidity (NTU)</td>
<td>105</td>
</tr>
<tr>
<td>Conductivity (µs/cm)</td>
<td>37080</td>
</tr>
<tr>
<td>Chloride (mg/l)</td>
<td>2513</td>
</tr>
<tr>
<td>Nitrate (mg/l)</td>
<td>1.2</td>
</tr>
<tr>
<td>Sulphate (mg/l)</td>
<td>9.8</td>
</tr>
<tr>
<td>TDS (mg/l)</td>
<td>18500</td>
</tr>
<tr>
<td>DO (mg/l)</td>
<td>6.10</td>
</tr>
<tr>
<td>Iron (mg/l)</td>
<td>11.8</td>
</tr>
<tr>
<td>TMC (cfu/ml)</td>
<td>10^4</td>
</tr>
</tbody>
</table>

TDS (Total Dissolved Solids); DO (Dissolved Oxygen).

Table 3: Measured temperatures in the two batch reactors

<table>
<thead>
<tr>
<th>Exposure time (hrs)</th>
<th>Reactor 1 (°C)</th>
<th>Reactor 2 (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>26.3</td>
<td>26.4</td>
</tr>
<tr>
<td>672</td>
<td>26.7</td>
<td>26.8</td>
</tr>
<tr>
<td>1008</td>
<td>27.1</td>
<td>27.1</td>
</tr>
<tr>
<td>1344</td>
<td>27.2</td>
<td>27.2</td>
</tr>
<tr>
<td>1680</td>
<td>26.5</td>
<td>27.1</td>
</tr>
<tr>
<td>2016</td>
<td>27.3</td>
<td>26.8</td>
</tr>
</tbody>
</table>

Corrosion rate (mpy) = \(\frac{AM \times 3.45 \times 10^6}{At}\) (1)

where \(AM\) 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).

Temperature and total microbial count (TMC) in the two batch reactors were measured throughout the test period, where temperature was measured using a multi-parameter water quality monitor (Model, 600 UPG), and TMC was determined using the rapid agar dipstick technique.\(^{(16)}\)

RESULTS AND DISCUSSION

The temperature in the two batch reactors varies from 26.3°C to 27.3°C (see Table 3), which is consistent with the temperature range 25°C - 30°C for microbial growth.\(^{(20)}\)

Figure 1 shows the variation of total microbial count with time in the two reactors. The TMC in reactor 1 decreases drastically from 10^4 to zero after 672 hours and maintained at this level throughout the remaining period of the experiment, while the TMC in reactor 2 increases tremendously from 10^4 to 10^6 cfu/ml within 672 hours and maintained at an average level of about 10^7 cfu/ml for the rest of the test period. The drastic reduction of TMC in reactor 1 is due to the biocide which eliminated the microorganisms in this reactor after 672 hours, while the drastic increase of TMC in reactor 2 is attributable to growth of microorganisms in this reactor resulting from continuous supply of nutrients by the fertilizer.

Figure 2 shows the variation of corrosion rate of coupon with time in the two batch reactors from which it may be seen that the corrosion rate in reactor 2 is higher than that in reactor 1. Earlier work by Costello\(^{(23)}\) indicates that microorganisms can cause corrosion rate to increase by about 1000 - 100,000 times greater than in the absence of microorganisms, and microbial corrosion has the potential to produce extra-ordinary corrosion rate of 25mpy.\(^{(22)}\) However, the microbial corrosion in the present study is greater than the non-microbial corrosion by about 94% and the maximum microbial corrosion rate obtained in the present analysis is 2.08mpy; this may depend on the types of microorganisms in the produced water, the nutrient-supplement used, and whether or not corrosion inhibitory elements are present in the produced water.

The corrosion rates in reactor 1 (without microorganisms) may be due to chemical components of the produced water like chloride, sulphate, nitrate, and iron (see Table 2). Also, the low corrosion rates in reactor 1 probably indicate the presence of corrosion inhibitory elements in the produced water which would also affect the corrosion rates in reactor 2. The key feature for enhancement of corrosion in reactor 2 is the presence of deposit (biofilm) on the metal surfaces. The nature of X60 coupon retrieved from reactor 1 (without microorganisms) after 2016 hours is shown in
Fig. 2: Variation of corrosion rate of coupon with time.

Fig. 3: Corrosion coupon after 2016 hours of exposure to produced water treated with 0.5ppm dissolved ozone (showing smooth surface without biofilm).

Fig. 4: Corrosion coupon after 2016 hours of exposure to produced water treated with NPK 15-15-15 fertilizer (showing biofilm on metal surface).

Fig. 5: Photograph showing pits on the surface of coupon retrieved from reactor 2 after 2016 hours when deposits on the surface have been removed.

Fig. 6: Illustrates the mass-loss of coupon retrieved from both reactors during the period of the experiment, indicating non-linear relationship between $\Delta M$ and $t$. The mass-loss of coupon is greater in reactor 2 than reactor 1, which is expected and is due to the higher corrosion rate in reactor 2 than reactor 1. When log of mass-loss is plotted against time for both reactors, an approximate linear relationship is obtained (see Fig. 7), confirming a first-
order chemical reaction in both reactors. This method of using a linear relationship between log of mass-loss and time to determine the order of a chemical reaction is reported in the literature.\cite{23,25}

**Conclusion:** An experimental study on the microbial and non-microbial corrosion of X60 steel immersed in produced water is presented. It is shown that the metal corrodes with or without microorganisms in the produced water. Corrosion of X60 steel in the absence of microorganism may be due to chemical components of the produced water like chloride, sulphate, nitrate, iron, etc. The influence of microorganisms is significant and results to about 94% increase in the corrosion rate of X60 steel when NPK-15-15-15 fertilizer is used as nutrient-supplement for the microorganisms in the produced water. The low corrosion rates of the metal in reactor 1 (without microorganisms) may indicate the presence of corrosion inhibitory elements in the produced water which would also affect the measured corrosion rates in reactor 2; this is not investigated in the present analysis and remains the focus of continuing work. The corrosion induced chemical reaction in both reactors is first-order, and microbial corrosion results in pinhole-size pits on the surfaces of the metal.

**REFERENCES**