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CORROSION OF X60 STEEL INFLUENCED BY IRON OXIDIZING BACTERIA (*LEPTOTHRIX DISCOPHORA*)

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ABSTRACT

Laboratory analysis of X60 steel coupons immersed in two separate batch reactors 1 and 2 containing formation water, with reactor 1 inoculated with *Leptothrix discophora* for a period of 84 days is presented It is shown that *Leptothrix discophora* influenced corrosion rate of X60 steel by about 123 percent, and the reaction between the microorganism and the metal is first-order Pinhole size pits were observed on the surfaces of coupons retrieved from batch reactor 1 after removing the biofilm on the surfaces of the coupons

KEYWORDS: Microbes, corrosion, X60 steel, formation water, *Leptothrix discophora*

1. INTRODUCTION

In the past few decades, the influence of microorganisms on the corrosion rate of metals has been the focus of corrosion experts Today, microbiologically influenced corrosion (MIC) has been reported in many systems, for example underground pipelines (Harris, 1960), drilling operations (Abu, 1992) marine structures (Videla, 1996), cooling water systems (Mittelman 2003) and waste water treatment facilities (Iversen 2001) It is estimated that about 20 percent of all corrosion damage of metals are MIC influenced or enhanced (Booth 1971) Damages resulting from microbial corrosion in production, transport, and oil storage facilities amount to hundred of millions US dollars per year in United States of America (Costerton and Boivin, 1991) 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 biofilms on a metal surface often leads to highly localized changes in the concentration of the electrolyte constituents, pH, and oxygen levels (Borenstein, 1991) 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 by destroying the protective film on 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 forms of corrosion such as pitting (Characklis and Cooksey, 1983) 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 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)

C (%)	Mn (%)	P (%)	S (%)	Cr (%)	Ni (%)	Mo (%)	V (%)	Cu (%)	Al (%)
0 199	1 59	0 016	0 018	0 015	0 007	0 008	0 004	0 024	0 024

In this work, results of laboratory studies on the corrosion rate of X60 steel in stagnant formation water are presented This investigation focuses on microbiologically influenced corrosion, and iron-oxidizing bacteria (*Leptothrix discophora*) is used on X60 pipeline steel coupons

2. MATERIALS AND METHOD

2.1. Materials

The materials used in the study are nutrient/culture medium, isolated strain of iron-oxidizing bacteria (*Leptothrix discophora*), X60 coupons, two (2) batch reactors, and formation water

2.1.1 Sample preparation

Culture medium

The culture medium used in the experiments contained (per litre of distilled water) 0.5g NH_4NO_3 (ammonium nitrate) 0 5g $NaNO_3$ (sodium nitrate), 0 5g K_2HPO_4, (potassium hydrophosphate) 0 5g $MgSO_4\,7H_2O$ (hydrated magnesium sulphate), 0 2g $CaCl_2\,6H_2O$ (hydrated calcium chloride), 10g ferric ammonium citrate, and 10g Agar powder The pH was adjusted to 7 0 – 7 2 by the addition of 50ml of 1M NaOH solution The culture medium was autoclaved at 121°C and a pressure of 1.2×10^{4} Pa. After sterilization, the medium was allowed to cool to room temperature before dispensing into 2 (two) petri dishes (see Fig.1).

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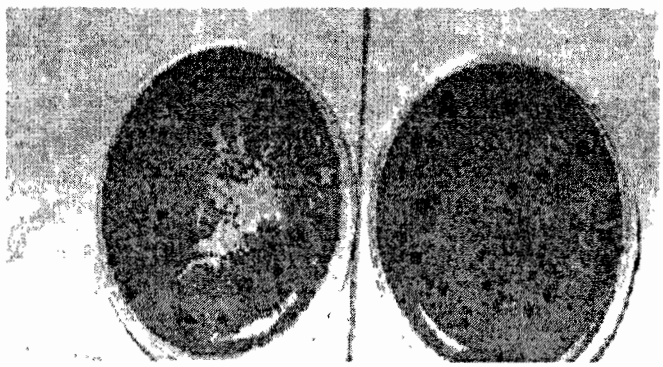

Fig 1 Colonized Leptothrix discophora

Leptothrix discophora strain

The seed bacteria (*Leptothrix discophora*) were aseptically isolated from New Calabar River by Wilbros Nig Ltd (a major service company), Port Harcourt The water sample was centrifuged and enriched in the prepared culture medium

Preparation of X60 Coupons

Sheets of X60 steel were obtained from Tricorr (Nig) Ltd , Port Harcourt, Nigeria, and cold cut to the dimensions $10\text{cm} \times 5\text{cm} \times 0.5\text{cm}$. The cold-cut technique was used so as to maintain the integrity of the steel and avoid probable effect of heat-affected zone (HAZ) on corrosion 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. Average weight of each prepared coupon ranges from 19.95 to 20.03g The exposed surface area of each coupon is 115cm^2 and is calculated as $2(Lw + Lh + hw)$, where $L = 10\text{cm}$ is the length of each rectangular coupon, $w = 5\text{cm}$ is the width, and $h = 0.5\text{cm}$ is the thickness (or height) of the coupon Forty (40) pieces of X60 steel coupons were prepared for the study.

2.2 Experimental method

Nine (9) litres of formation water collected from a flow station in Rivers State was equally divided into batch reactors 1 and 2, and inoculum of *Leptothrix discophora* was added to batch reactor 1 To provide nutrient for the microorganism, 2g of the culture medium was added to reactor 1 on weekly basis throughout the test period Into each of the batch reactors, 5 prepared X60 steel coupons were completely immersed and the experimental set-up was left for a test period of 4, 6, 8, 10 and 12 weeks At the end of each test period, a coupon was retrieved from each reactor washed, dried, and weighed Corrosion rate of X60 steel coupon was determined using the mass loss technique (Bradford, 1993) as

$$\text{Corrosion rate (mm/year)} = \frac{\Delta M \times 3.45 \times 10^6}{A\rho t} \quad (1)$$

where ΔM is the mass loss (g) of the coupon, A is the total exposed surface area of the coupon (cm^2), ρ is the density of the coupon (g/cm^3), and t is time (hours) Temperature, total microbial count (TMC) pH, and dissolved oxygen (DO), in the batch reactors were measured throughout the test period Note that temperature, pH, and DO, were measured using a multi-parameter water quality monitor (Model, 600 UPG) while TMC was determined using the rapid agar dipstick technique (Borenstein, 1995).

3. RESULTS AND DISCUSSION

Results of the experiments are presented in Table 2. The observed temperature range in both reactors (26.3°C - 27.6°C)

Table 2: Measured parameters in the two batch reactors

	Batch reactor 1				Batch reactor 2			
Exposure time (hrs)	pH	Temp (°C)	DO (mg/l)	TMC (cfu/ml)	pH	Temp (°C)	DO (mg/l)	TMC (cfu/ml)
0	5.8	26.4	8.40	10^3	5.8	26.3	8.30	10^3
672	6.2	26.6	5.42	10^6	6.3	26.4	5.40	10^2
1008	6.4	26.7	3.80	10^3	6.5	26.8	4.71	10
1344	5.5	26.8	2.10	10^3	6.6	26.9	4.09	<10
1680	5.7	27.3	1.02	10^4	6.7	27.1	3.70	<10
2010	5.8	27.6	0.71	10^3	6.8	27.5	3.20	<10

is suitable for the growth of *Leptothrix discophora*, where the optimal temperature for microbial growth is between 25°C and 30°C (Lee and Newman, 2003). pH values in both reactors during the test period is slightly acidic (between 5.5 and 6.8). DO level in batch reactor 1 varies between 8.40 and 0.71mg/l, while that in batch reactor 2 is between 8.30 mg/l and 3.20 mg/l. Variation of DO in the reactors is illustrated graphically in Fig. 2, showing that the rate of dissolved oxygen consumption in both reactors is close within 672 hours of the test period. As the reaction progresses, the DO level in reactor 1 reduces drastically, and this may be attributed to the presence of *Leptothrix discophora* which utilizes oxygen as a substrate. Similar observations have been made on the rate of oxygen consumption by immobilized nitrate oxidizing bacteria (*Nitrobacteria agilis*) in water environment (Picioreanu, *et al*, 1998)

Figure 3 illustrates the variation of total microbial count with time in the two reactors At the start of the experiment, the TMC in both reactors are the same (10^3 cfu/ml). In reactor 1, there was an observed increase in TMC from 10^3 to 10^6 cfu/ml within 672 hours of the experiment and maintained a fairly constant value of 10^3 cfu/ml throughout the rest of the test period. The observation in batch reactor 1 may be attributed to the transformation of initial planktonic cells to sessile cells despite the continuous supply of nutrients (Zhang and Dexter, 1995, Dexter and Gao, 1988). The drastic reduction of TMC in reactor 2 is due to depletion of nutrients in the medium. Corrosion rate of all coupons measured in batch reactors 1 and 2 are presented in Table 3 and depicted graphically in Fig. 4.

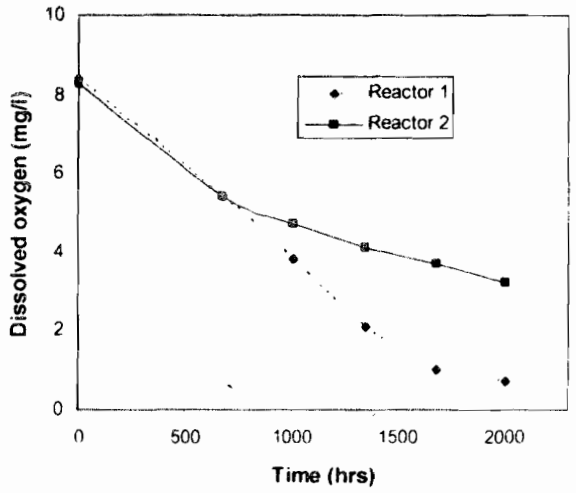

Fig. 2: Variation of dissolved oxygen with time

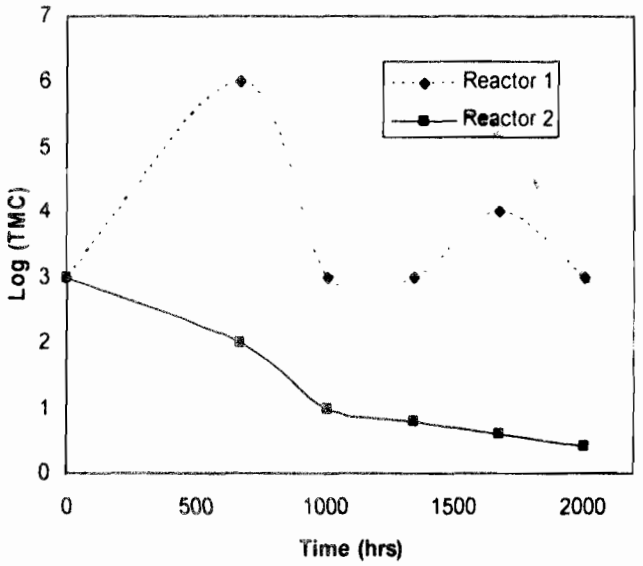

Fig. 3: Variation of TMC with time.

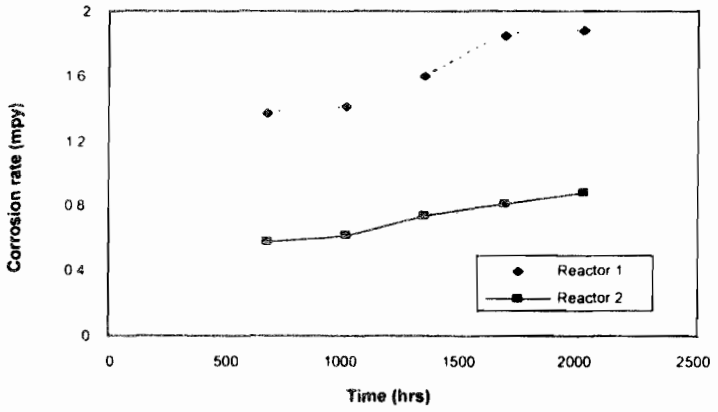

Fig. 4: Variation of corrosion rate of coupons with time.

Table 3 Corrosion rates of X60 steel in batch reactor 1 and 2

Exposure time (hrs)	Batch reactor 1		Batch reactor 2	
	ΔM (g)	Corrosion rate (mpy)	ΔM (g)	Corrosion rate (mpy)
672	0.24	1.37	0.10	0.58
1008	0.37	1.41	0.16	0.62
1344	0.56	1.60	0.26	0.74
1680	0.81	1.85	0.34	0.81
2016	0.99	1.88	0.47	0.88

Comparing the corrosion rates of coupons in both reactors shows that the corrosion rate of coupons immersed in batch reactor 1 are higher than those in batch reactor 2. These results confirm earlier observation (Costello, 1969) that the most direct effect of MIC is increase in corrosion rate, and that the presence of microorganisms can cause corrosion rate to increase by about 1000 – 100,000 times greater than in the absence of microorganisms. However, in this study, the presence of *Leptothrix discophora* enhances corrosion rates by about 123 percent. The key feature for the enhancement of corrosion in the present analysis is the alteration of the metal surfaces by the presence of rusty deposit (biofilms). Typical morphology of biofilm on the surfaces of the X60 coupon retrieved from reactor 1 (inoculated with *Leptothrix discophora*) after the exposure time of 84 days is shown in Fig. 5. The deposits present a thick rusty layer with discontinuous appearance. The nature of a surface of X60 coupon retrieved from reactor 2 (without the inoculum of *Leptothrix discophora*) after 84 days is shown in Fig. 6, where the appearance of the surface does not indicate the presence of mosaic deposit or biofilm. After removing the deposit formed on the surface of the coupon in Fig. 5, pinhole size pits were observed on the surface of the coupon (see Fig. 7) which is attributable to the activities of the microorganisms. The observed corrosion rates of coupons in batch reactor 2 may have resulted from the effects of the chemical compositions of the formation water

Fig. 5: **Morphology of biofilm on the surface of X60 steel coupon retrieved from batch reactor 1 after 84 days.**

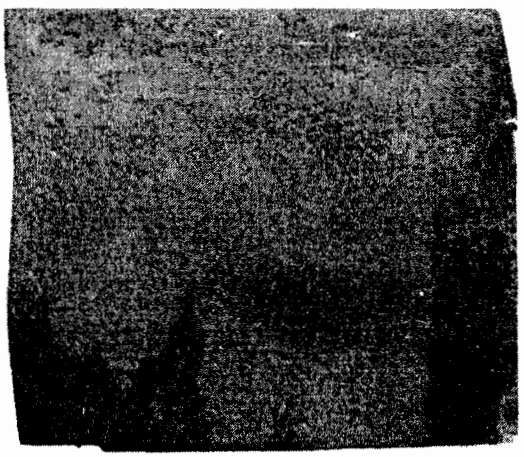

Fig. 6: **Photograph showing surface of X60 steel coupon retrieved from batch reactor 2 after 84 days.**

Fig. 7: Photograph showing pits on the surface of coupon retrieved from batch reactor 1 after 84 days.

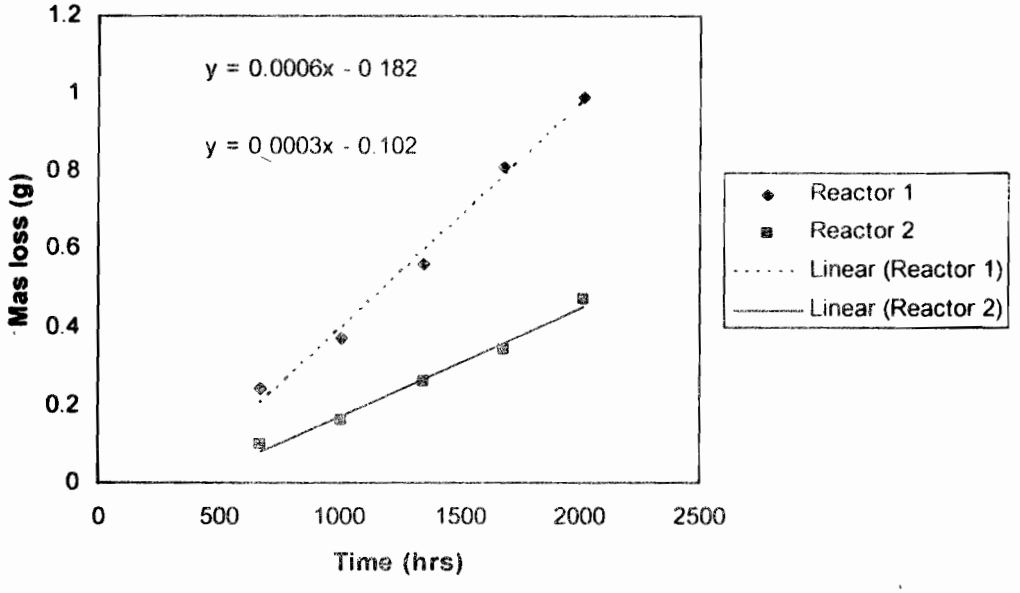

Fig. 8: Variation of mass loss of coupon with time.

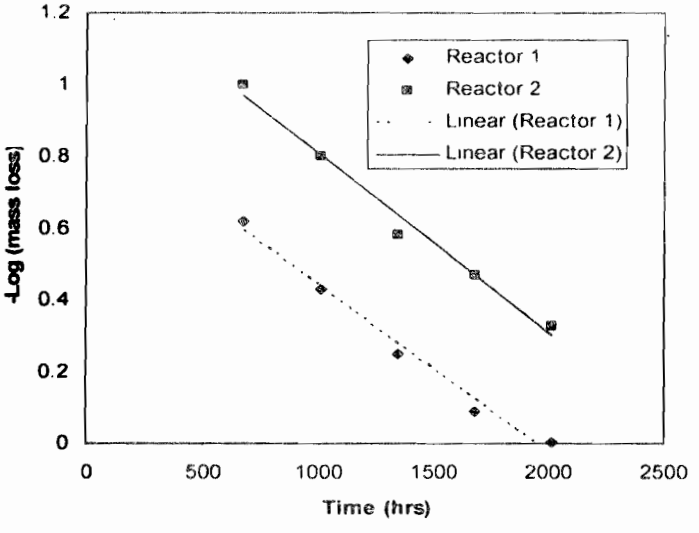

Fig. 9: Plot of Log (mass loss) of coupon against time.

Results of chemical analyses of the formation water used in the analysis are presented in Table 4, which are similar to those obtained by Rim-Rukeh (2005) on formation used in his study. The average value of each parameter shown in Table 4 was calculated from a set of 5 experimental readings. Figure 8 illustrates the mass loss of coupons in both reactors during the period of the experiment, indicating approximate linear relationship between ΔM and t as obtained by Uhlig (1948) in the form

$$\Delta M = kt \qquad (2)$$

where k is a proportionality constant that depends on the conditions in a specific environment. Figure 8 shows increase in mass loss of the coupons in both reactors with time, which is more pronounced in reactor 1 than reactor 2. The corrosive aggressiveness in reactor 1 is due to the presence of *Leptothrix discophora*. It may be seen from the trend lines in Fig. 8 that $k = 0.0006$ (with an error of about 18%) in reactor 1, and $k = 0.0003$ (with an error of about 10%) in reactor 2. When the log of mass-loss is plotted against time for both reactors, an approximate linear relationship is obtained (see Fig. 9), confirming a first-order chemical reaction between the microorganism and the metal. This method of using a linear relationship between log of mass-loss and time in determining the order of a reaction is reported in the literature (Jones, 1988; Omo-Odudu and Oforka, 1999; Rim-Rukeh, 2005). It is interesting to observe from Fig. 9 that, the condition in reactor 2 also conforms approximately to first-order kinetics, indicating chemical reaction between components of the formation water and the metal.

Table 4 Chemical composition of formation water.

Parameter	Average value
pH	5.3
Turbidity (NTU)	71
Conductivity (µs/cm)	9100
Chloride (mg/l)	2513
Nitrate (mg/l)	42.5
Sulphate (mg/l)	Nil
TDS (mg/l)	8509
DO (mg/l)	8.40
Iron (mg/l)	16.7
Manganese (g/l)	0.18

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

4. CONCLUSION

Laboratory analyses on corrosion of X60 steel coupons immersed in formation water inoculated with iron-oxidizing bacteria (*Leptothrix discophora*), and without the bacteria, have been presented. It is shown that *Leptothrix discophora* increases the rate of corrosion of the metal by about 123 percent, and the corrosion of X60 steel in the presence of the bacteria follows a first-order kinetics. MIC (in the presence of *Leptothrix discophora*) results in the formation of patchy biofilm on the metal surface which may be attributed to differential aeration of the surface.

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