

## MICROBIAL CORROSION OF MILD AND MEDIUM CARBON STEELS

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### Abstract

The role of bacteria in the corrosion of mild and medium carbon steels is reported. The steels were exposed to anaerobic and aerobic, and fresh water (control) environments. The corrosion rates were evaluated at intervals of seven days for a period of 42 days using weight loss and electrochemical methods. The corroded specimens were visually examined and majorities were found to have undergone general corrosion in the three environments (aerobic, anaerobic, and fresh water). The mild steel was found to corrode more than the medium carbon steel in anaerobic environment-mild steel:  $6.43 \times 10^{-4}$  mpy and -0.93 mV, due to limited available oxygen whilst it had -0.89 mV in aerobic and -0.77 mV in the fresh water. The medium carbon steel had  $-5.30 \times 10^{-4}$  mpy and -0.91 mV in anaerobic: -0.84mV in aerobic and -0.74mV in freshwater.

Keywords: Bacteria, Corrosion, Carbon steel, Freshwater.

### 1. Introduction

Corrosion due to the activities of micro-organisms is referred to as microbial corrosion. These organisms are involved in the corrosion process by the virtue of their growth and metabolic actions and their presence often provide concentration cells in the structure where they are present, whereby some areas in the structure are anodic to the rest. These bacteria are therefore classified into two- those that require oxygen in the metabolic and growth processes often referred to as aerobic bacteria and those that carry out their activities in the absence of oxygen often referred to as anaerobic [1]. These bacteria are active in stagnant water mainly at bottom of tanks, the soil, freshwater, seawater and air.

The mere detection of sulphur reducing bacteria (SRB) does not constitute a problem but what is important is the number of micro-organisms of the relevant

**Nomenclatures**

$A$	Total surface area of coupons, $\text{cm}^2$
Cfu/ml	Colony forming units per millimetre
$\text{CO}_2$	Carbon-dioxide
CR	Corrosion rate, mpy
Cu/CuSO <sub>4</sub>	Copper/ Copper sulphate reference electrode
$D$	Density, $\text{g}/\text{cm}^2$
$D_h$	Diameter of hole on specimen, cm
$e^-$	Electron
Fe	Iron
Fe(OH)	Ferrous Oxide
FS	Iron sulphide
$H$	Thickness of specimen, cm
$\text{H}^+$	Hydrogen ion
$\text{H}_2\text{O}$	Water
$L$	Length, cm
$\text{OH}^-$	Hydroxy ion
pH	Measure of acidity and alkalinity of a solution
$\text{S}^-$	Sulphide ion
$\text{SO}_4^{2-}$	Sulphate ion
$T$	Exposure time, hours
$W$	Width of specimen, cm
WT.LOSS	Weight loss, g

**Abbreviations**

Ep	Electrode Potential
MCS	Medium carbon steel
mpy	Mill per year
MS	Mild steel
SRB	Sulphur reducing bacteria

types generated. It has been observed that under favourable conditions, bacteria can multiply every 10- 60 minutes in their metabolic and growth process up to  $2.8 \times 10^{14}$  organisms which lead to the corrosion and biodeterioration of materials. However, this growth and reproduction process is generally reduced after the first bloom since conditions progressively become inhibitory; predators become evident [1]. These organisms thrived in medium with pH values between 0 and 11, temperature between 0 and  $80^\circ\text{C}$  (30 and 180 F) and under the pressure of up to 103 MPa (15 ksi). The activities of bacteria are affected by the availability of nutrient e.g. phosphate, nitrogen, and presence of toxic substances (oxygen for sulphate reducers, chlorine, biocides). SRB is the most important group of bacteria associated with this form of corrosion and it is widely believed that all microbial- induced failures are due to its activities. SRB are anaerobic and heterotrophic, i.e., they obtain their energy from organic nutrients [1-11].

Their respiratory utilizes sulphate, which is abundant in fresh water, sea water and soils and often results in the formation of hydrogen sulphide. This hydrogen sulphide appears as  $\text{H}_2\text{S}$  (in the dissolved or gaseous form).  $\text{HS}^-$  ions,  $\text{S}^{2-}$  ions or metal sulphides, or a combination of these according to the prevailing conditions.

The SRB in the presence of organic materials is oxidized to form the sulphide [12-28]



The sulphide is highly corrosive to most engineering materials. The most commonly encountered SRB is desulfovibrio. In the industrial process plant, a wide range of bacteria such as pseudomonas and falvo bacterium exist. These can secrete large amount of organic material under both aerobic and oxygen free (anaerobic) conditions. The petroleum industry has been plagued by the activities of bacteria (SRB) because it handles large volumes of deaerated water from underground reservoirs.

Aerobic bacteria grow due to the assimilation of  $\text{CO}_2$ , by using the energy derived from the oxidation of sulphur, sulphate, thiocyanate, and trio and tetra-athionate for their growth. These are chemolithotrophs or autotrophs, i.e., the ability to grow on  $\text{CO}_2$  as opposed to chemo-organotrophs whose energy for growth is from organic materials. The aerobes that cause this type of corrosion are the bacillus of which thiobacillus and thio-oxidans are examples. They are generally found in sulphur-bearing organic waste product, in soil and water with low pH in the immediate vicinity [29-34].

The thiobacilli oxidizes the elemental sulphur to produce sulphuric acid as shown in the reaction below:



The present study was undertaken to quantitatively determine the corrosion of medium and high carbon steel in aerobic and anaerobic conditions.

## 2. Materials and Methods

### 2.1. Materials

The mild and medium carbon steels were obtained from Delta steel Company Limited, Ovwian-Aladja, Delta State, Nigeria. They were in forms of rods of diameter of 12 mm and were cut to coupons of nominal dimensions of 73×22×5 mm using a hacksaw blade. All cut edges were grinded to produce a good surface, finishing with emery cloths of different grades. A hole of diameter 7.0 mm was drilled on the steel coupons to enhance their ease of suspension in the different media.

The chemical compositions of the steels as supplied by the manufacturer are given in Table 1.

**Table 1. Chemical Composition of the Steels as Supplied by the Manufacturer.**

Steel Grade	C	Si	Mn	Cu	P	S	Cr	Ni	Sn	Fe
MS (wt %)	0.18	0.23	0.80	0.20	0.03	0.04	0.05	0.55	0.02	Bal.
MCS (wt %)	0.40	0.25	0.52	0.05	0.03	0.02	-	-	-	Bal.

Key: MS = Mild Steel, MCS = Medium Carbon Steel.

## 2.2. Preparation of the environments

Three environments were used in this research;

- (i) Anaerobic sulphur reducing bacteria.
- (ii) Aerobic sulphur reducing bacteria, and
- (iii) Fresh water (control).

## 2.3. Preparation of bacterial environment

5g of sulphur was measured and buried in the soil for seven days. The sulphur powder mixed with soil sample was collected after seven days. Then, 1g of the soil was weighed and serially diluted. Nutrient agar medium was prepared by mixing the compositions in Table 2 and was added to 1g of sulphur and allowed to solidify. 0.1ml of the fifth serially diluted soil sample was pipette on the nutrient agar plate. It was spread with a spreader and incubated anaerobically. The bacterial of the genera *desulphurvibrio* was isolated from anaerobic incubation. The freshwater was obtained from a borehole within the university environment.

**Table 2. Composition of Nutrient Algae used for the Preparation of the Bacterial Environment.**

Compound	NaCl	MgSO <sub>4</sub> ·7H <sub>2</sub> O	KCl	KH <sub>2</sub> PO <sub>4</sub>	Na <sub>2</sub> HPO <sub>4</sub>	NaNO <sub>3</sub>	Agar
Composition (g)	10	0.3	0.29	0.83	1.25	0.42	12.5

## 2.4. Experimental Procedure

### 2.4.1. Corrosion rate measurement

The corrosion rate of the coupons was monitored by total immersion/weight loss technique and electro-potential method. The coupons were cleaned and dried in acetone before immersion. The initial weights of the coupons were taken with a digital electronic weighing machine (contech) to the nearest 0.001g and were noted. The samples were then totally exposed to the environments containing aerobic and anaerobic sulphur reducing bacteria.

Suspension was done with the aid of a rubber thread which passes through the hole in each coupon. The initial electro-potential of each of the coupons was taken using the copper/copper sulphate (Cu/CuSO<sub>4</sub>) reference electrode connected to a digital multi-meter of the model DT 9205, and the results were noted. A coupon was removed from each media each week till the end of the experiment.

The coupons were removed from the environments at interval of seven days. The oxide film formed on the surface of the coupons were examined visually, brushed with a sponge in tap water and then dipped in acetone and then dried.

The final weight of the test specimen removed from the control and other environments was taken and recorded using electronic weighing machine. The coupons were then discarded. The procedure was repeated at intervals of seven days for a total period of six weeks (42 days).

### 2.4.2. Visual examination

Samples were carefully examined visually during each monitoring day with the aim of identifying:

- (i) The type of substances or the nature of the oxide scales on the surface of the specimens.
- (ii) The type of corrosion occurring.
- (iii) Any changes in the colour of the corrosion products.

### 2.4.3. Chemical test

Chemical test was carried out to indicate the type of corrosion. This was done by gently scrapping the corroding surface and putting it in a test tube. Concentrated hydrochloric acid (HCl) was then added to it. The mixture was heated in a gas burner.

### 2.4.4. Bacteria concentration and pH of the environment

The bacteria concentrations in colony forming units per milliliter (cfu/ml) were taken at an interval of seven days for a period of six weeks using colony counter. Bacterial concentration increases with exposure time (days). The pH of the environment was taken along each time potential readings were taken. The pH readings were made using a pH meter (MAC Type).

## 3. Experimental Results

### 3.1. Weight loss

The corrosion behavior of mild and medium carbon steels in aerobic, anaerobic environments and in distilled water which serves as a control was studied by monitoring the electro-potential and weight loss of the specimens at intervals of seven days.

The results of the weight losses of the steel coupons were converted to corrosion rate in penetration per year and are given in Table 3 and plotted in Figs. 1 to 6.

### 3.2. Corrosion rate

The corrosion rates of steels using weight loss method in the various environments were calculated using the formula [2]

$$CR = 534W/DAT \quad (3)$$

where, CR is the corrosion rate in mill per year (mpy),  $W$  is the weight loss in grams (g),  $D$  is the density of steel ( $\text{g/cm}^3$ ),  $A$  is the total surface area ( $\text{cm}^2$ ), and  $T$  is the exposure time in hours (hrs).

The results are given in column 2 of Table 3 for each week. Details of calculation are shown in *Appendix A*.

### 3.3. Potential measurement

The corrosion rate measurement was made using the electrical properties of a corroding system. For a corroding system the electrical potential and consequently the current and resistance are affected [36].

Using Ohm's law

$$V = IR \quad (4)$$

where  $V$  is the potential in voltage,  $R$  is the resistance in ohms and  $I$  is the current in Amperes.

The voltage decreases as the resistance increases due to the corrosion product formed on the steel surface. Hence, the lower the potentials, the more the corrosion is.

### 3.4. Chemical test results

A colourless gas with a rotten egg odour evolved with a black residue of iron II chloride. The rotten egg odour of  $H_2S$  indicated that SRB was responsible for the corrosion of these steels.



### 3.5. Visual examination

The steel samples exposed to the various environments were examined visually. General (uniform) corrosion and pitting were observed for all the steel samples exposed to aerobic, anaerobic and the control.

## 4. Results and Discussion

The corrosion rate of mild steel and medium carbon steels depends on several corrosion parameters such as chemical composition, surface finish, and pH. Anaerobic, aerobic and fresh water contain corrosion inducing ions such  $OH^-$  and  $SO_4^{2-}$ . Therefore these environments are considered aggressive and toxic to most engineering materials including steel.

Relating between laboratory test, chemical analysis, and visual examination, the results of the investigation are discussed under the following headings: weight loss of sample, and corrosion rates measurement.

### 4.1. Weight loss of sample

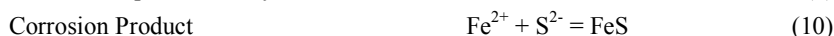
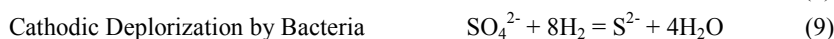
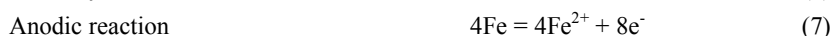
Figure 1 shows the weight loss of the steel samples as a function of the environment and exposure time (days). Mild steel and medium carbon steel were found to corrode in different environment containing SRB investigated, and this was evidenced by the decrease in the original weight (weight loss).

Mild steel has the highest weight loss in all the environments investigated; recorded (156 mg) in anaerobic, (130 mg) in aerobic environment and (82 mg) in

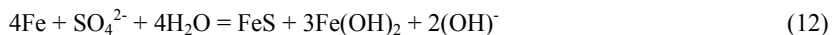
the control. As could be seen in Table 4 and Fig. 1, the weight loss of mild steel coupons in all the environments increased within the first 28th days. This observation was attributed to the fact that the rate of a chemical reaction increases with time [16, 35]. However, between the 35th and 42nd days of the investigation, mild steel in all the environments showed a sharp decrease in weight loss with time. This behaviour could be explained from the concept of passivation [2, 36].

Medium carbon steel has the least weight loss, recorded (136 mg) in anaerobic, (98 mg) in aerobic environment and (76 mg) in the control. It was generally observed (Table 5 and Fig. 1) that the weight loss of medium carbon steel coupons in the entire environment increased with time in the first 28th days. Also, between the 35th and 42nd day of the investigation, medium carbon steel in all the environments showed sharp decrease in weight loss with time. These observations are attributed to the same behaviour reported for mild steel above.

The higher weight losses associated with anaerobic environment was partly due to the high rate of permeability and diffusion of corrosion-inducing agents such as OH<sup>-</sup> and SO<sub>4</sub><sup>2-</sup> ions through the protective barrier oxide film formed, while in aerobic environment the rate of permeability and diffusion of these corrosion-inducing ions is slow. The presence of SO<sub>4</sub><sup>2-</sup> ion which is reduced by SRB to produce H<sub>2</sub>S, ferrous sulphide and other corrosion products can be illustrated in the following equations:



Overall Reaction becomes



The corrosion products such as FeS and 3Fe(OH)<sub>2</sub> do not form protective layers as discussed earlier, hence continuation in the corrosion process.

## 4.2. Corrosion rate measurement

### (i) Weight loss method:

The corrosion rate was higher for mild steel, followed by the medium carbon steel. It was generally observed (Fig. 2) that corrosion rate decreases with exposure times in all the environments. This experimentally observed behaviour was due to the formation of an impermeable protective oxide film on the surface of the steel. In this state, the steel is said to be passive [36-38] and does not corrode easily.

Mild steel corroded more than medium carbon steel in the first 28<sup>th</sup> days due to high rate of permeability of corrosion inducing agents such as OH<sup>-</sup> and SO<sub>4</sub><sup>2-</sup>, while after 28<sup>th</sup> days the aggressive ions in the various environments could not

be absorbed by the protective oxide film, hence the decrease in the corrosion rate with higher exposure times for all the environments studied. When steel is exposed to a corrosive environment there is usually rapid corrosion, but this decreases with time due to the formation of corrosion products which may be oxides, sulphates, carbonates or nitrides. If this product is not removed from the surface of the steel the corrosion rate is reduced. In this study, the corrosion inducing agents ( $\text{OH}^-$  and  $\text{SO}_4^{2-}$ ) could not easily diffuse through the corrosion products formed on the steel surfaces at exposure times greater than the 28<sup>th</sup> days. The time taken by the corrosion inducing agents to diffuse through the oxide (corrosion products) to the steel, i.e., the base metal contributed significantly to the observed difference in the corrosion rates. These observations are in qualitative agreement with Ovri, [2, 23, 36] on steel reinforcements in concrete and ferrite.

### (ii) Electro-chemical method:

The plot of the electrode potentials with exposure times of the steel coupons in all the environments investigated is given in Fig. 2. It was observed that the electrode potential of the steel exposed to all the environments decreased with time during the first 28<sup>th</sup> days of the investigation and later increased till the end of the study. The electrode potential (voltage) decreased as resistance increased due to corrosion product formed on the steel surface [36, 39]. Hence, the lower the potential, the more the corrosion.

Mild steel in anaerobic environment recorded the highest decrease in electrode potential in the first 28<sup>th</sup> days of the study. It had initial potential of -0.47 mV in the first day and -0.93 mV in the 28<sup>th</sup> days. This decrease in electrode potential shows increase in corrosion rate and weight loss. However, a sharp increase in electrode potential occurred from the 35<sup>th</sup> to the 42<sup>nd</sup> days (-0.86 mV to -0.85 mV), showing a decrease in the corrosion rate. This effect is similar to all results obtained for mild steel in aerobic and the control environment.

Medium carbon steel in anaerobic environment was next after mild steel. It had -0.66 mV in the first day and -0.91 mV in the 28<sup>th</sup> day which is an indication of increase in corrosion rate. However, the electrode potential increased from -0.83 mV to -0.82 mV in the 35<sup>th</sup> to 42<sup>nd</sup> days respectively, showing decrease in corrosion rate and weight loss. This effect is similar to all results obtained for medium carbon steels in aerobic environment and the control.

The observed increase in electrode potential after 28 days of the test was attributed to the concept of passivity. This was caused by the formation of protective oxide film on the surface of the steels. Due to chemical, physical and electronic properties of these oxide films, metal dissolution is lowered resulting to the decrease in corrosion rate. The mild steel in anaerobic environment exhibited lowest electrode potential (highest negative potentials) indicating both high weight losses and corrosion rate, followed by aerobic and control respectively.

The results are in agreement with those reported by Owate, et al. [16] for the corrosion of mild and high carbon steels.



**(iii) The pH:**

The pH decreased in the first 28th days indicating high corrosion rate and weight loss. It could be seen in Fig. 6 that weight loss increased as the pH is decreased (lowered) making the environment more acidic and consequently more corrosive. However, between the 35th and 42nd days, the pH increased. This is due to the presence of protective oxide film that passivate the steel surface. The passivity of steel is reduced as the pH is increased [16].

**Table 3. Weight Loss (g), Corrosion Rate (mpy) and Potential (mV) in Various Environments.**

	Weight Loss Method													
	0 day		7 days		14 days		21 days		28 days		35 days		42 days	
	Wt Loss (g)	CR (mpy)	Wt Loss (g)	CR (mpy)	Wt Loss (g)	CR (mpy)	Wt Loss (g)	CR (mpy)	Wt Loss (g)	CR (mpy)	Wt Loss (g)	CR (mpy)	Wt Loss (g)	CR (mpy)
Control MCS	0.00	0.00	0.030	2.94	0.051	2.50	0.076	2.35	0.076	1.86	0.076	1.49	0.074	1.21
Control MS	0.00	0.00	0.042	4.15	0.069	3.41	0.076	2.60	0.082	2.03	0.080	1.58	0.078	1.29
Anaerobic MCS	0.00	0.00	0.054	05.30	0.088	4.31	0.125	4.08	0.136	3.33	0.132	2.59	0.128	2.09
Anaerobic MS	0.00	0.00	0.065	6.43	0.098	4.84	0.140	4.61	0.152	3.76	0.150	2.95	0.140	2.31
Aerobic MCS	0.00	0.00	0.49	5.00	0.076	3.72	0.089	2.91	0.098	2.40	0.083	1.76	0.085	1.40
Aerobic MS	0.00	0.00	0.053	5.24	0.084	4.15	0.105	3.46	0.130	3.21	0.120	2.37	0.116	1.91

	Electrode Potential Method						
	0 days	7 days	14 days	21 days	28 days	35 days	42 days
	EP (mV)	EP (mV)	EP (mV)	EP (mV)	EP (mV)	EP (mV)	EP (mV)
Control MCS	-0.47	-0.65	-0.70	-0.74	-0.74	-0.72	-0.73
Control MS	-0.55	-0.67	-0.73	-0.76	-0.77	-0.74	-0.74
Anaerobic MCS	-0.66	-0.77	-0.83	-0.90	-0.91	-0.83	-0.82
Anaerobic MS	-0.70	-0.83	-0.87	-0.95	-0.93	-0.86	-0.85
Aerobic MCS	-0.54	-0.70	0.77	-0.82	-0.84	-0.76	-0.75
Aerobic MS	-0.62	-0.75	-0.81	-0.88	-0.89	-0.79	-0.79

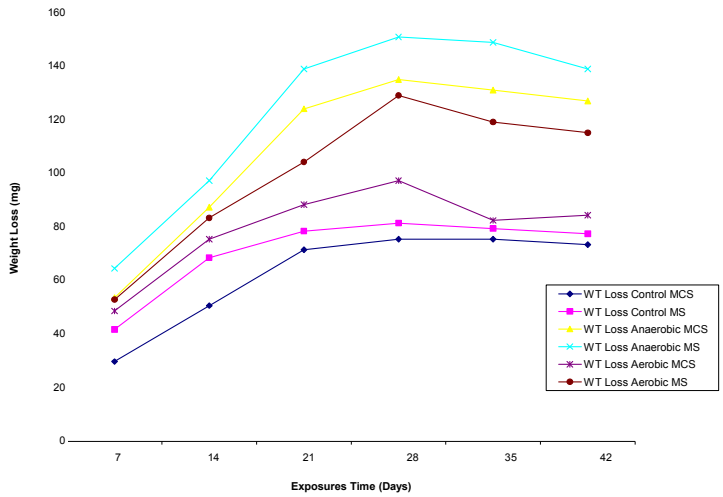
Key: Env.- Environment, Wt. Loss - Weight Loss, CR- Corrosion Rate, EP – Electropotential.

**Table 4. Results for pH Measurement in Anaerobic, Aerobic and the Control Environments.**

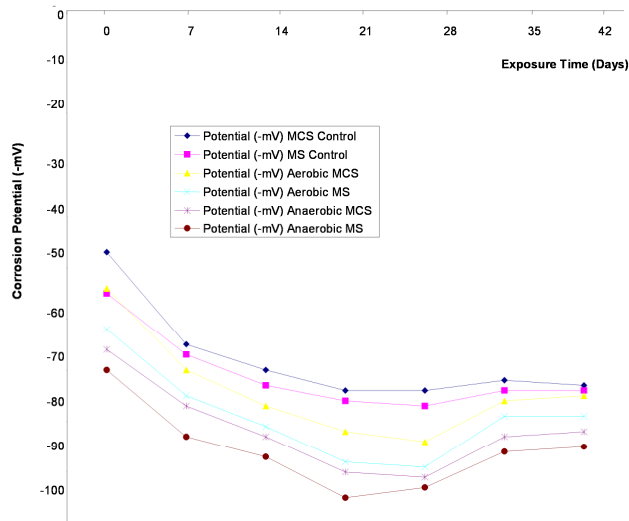
Environment	pH 0-day	7-day	14-day	21-day	28-day	35-day	42-day
Control	6.90	6.72	6.40	5.78	5.78	6.32	6.80
Anaerobic	6.80	6.05	5.50	5.00	4.50	5.50	6.00
Aerobic	6.85	6.40	6.35	5.25	5.00	6.00	5.85

**Table 5. Results of Bacterial Concentration of Anaerobic and Aerobic Environments.**

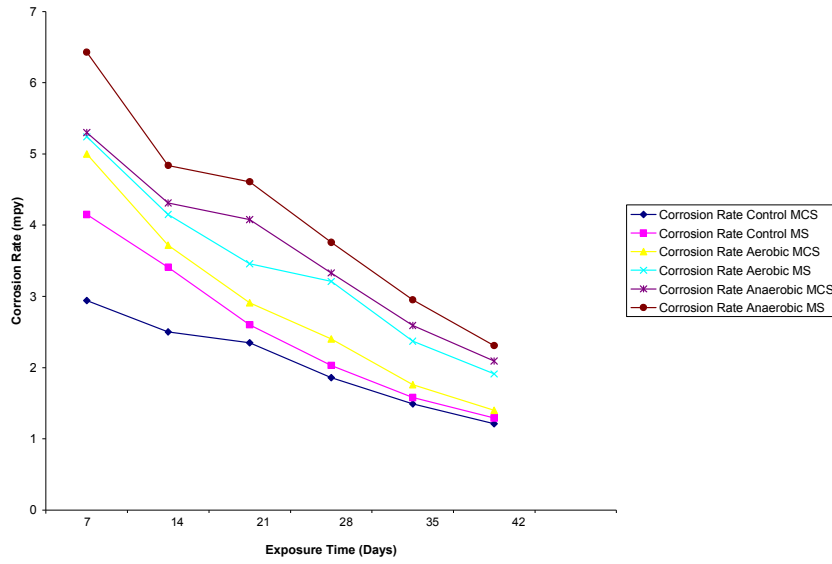
Bac.Conc	0-day	7-day	14-day	21-day	28-day	35-day	42-day
Anaerobic (cfu/ml)	300	350	400	450	500	530	550
Aerobic (cfu/ml)	200	250	300	350	380	400	450



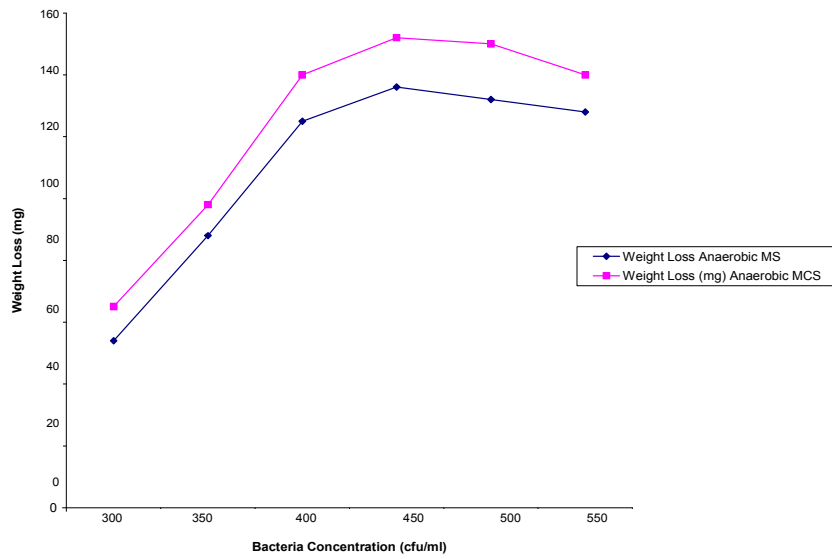
**Fig. 1. Variation of Weight Loss in (mg) with Exposure Time in (days) for Steel Coupons Exposed to Aerobic, Anaerobic and the Control.**



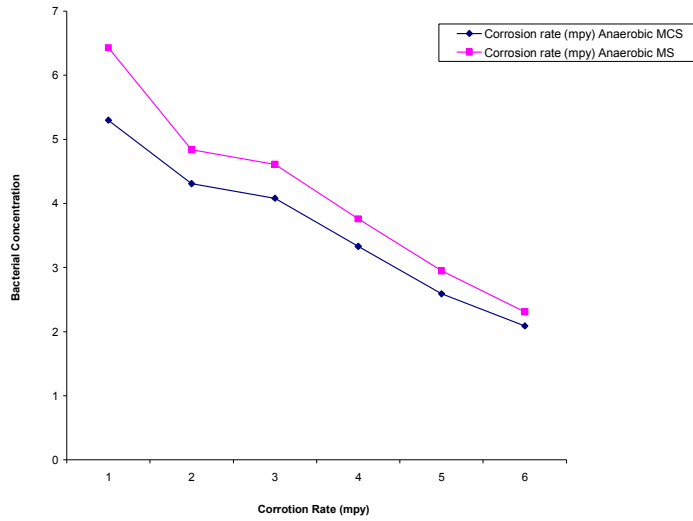
**Fig. 2. Variation of Potential (-mV) with Exposure Time (days) for Steel Coupons Exposed to Aerobic, Anaerobic and the Control.**



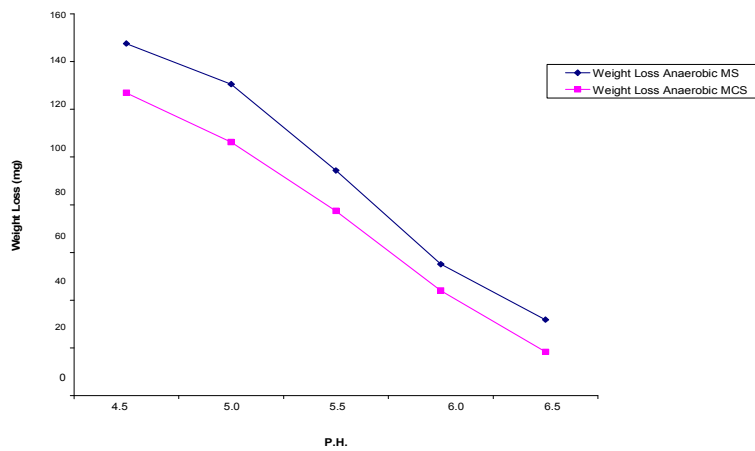
**Fig. 3. Variation of Corrosion Rate in (mpy) with Exposure Time (days) for Steel Coupons Exposed to Aerobic, Anaerobic and the Control.**



**Fig. 4. Variation of Weight Loss in (mg) with Bacteria Concentration (cfu/ml) for Steel Coupons Exposed to Anaerobic Environment.**



**Fig. 5. Variation of Bacterial Concentration with Corrosion Rate for Steel Coupons Exposed to Anaerobic Environment.**



**Fig. 6. Variation of Weight Loss with pH for Steel Coupons Exposed to Anaerobic Environment.**

### 5. Conclusions

The following conclusion can be drawn from this investigation:

- Mild steel was observed to be more corrosive in the entire environments ( $6.43 \times 10^{-4}$  mpy). This is due to high rate of permeability of corrosion inducing agents such as  $\text{OH}^-$  and  $\text{SO}_4^{2-}$ . This was followed by medium carbon steel ( $5.30 \times 10^{-4}$  mpy) with low rate of diffusion of the corrosion agents.

- General (uniform) corrosion was observed for mild and medium carbon steels in the entire environments investigated.
- The passivity of the steels is reduced as the pH is lowered.
- It has been shown that corrosion rate tends to decrease with increasing carbon content.
- Based on these results, medium carbon steel is suggested for use in oil industries when the environment contains SRB.

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### *Appendix A*

#### **Calculation of the Corrosion Rate**

The total surface area,  $A$ , of the rectangular steel coupons used in the investigation was calculated using the following relationship.

$$A = 2(LW + LH + WH) - 2\pi D_h^2/4$$

where

$A$ is the total surface area of coupons, cm <sup>2</sup>	
$L$ is the length =	7.30 cm
$W$ is the width =	2.20 cm
$H$ is the thickness =	0.5 cm
$D_h$ is the diameter of holes =	0.7 cm

$$A = 2(7.3 \times 2.2 + 7.3 \times 0.5 + 2.2 \times 0.5) - (3.142 \times (0.7)^2/4)$$

$$= 2(16.06 + 3.65 + 1.10) - 2(0.385) = 40.85 \text{ cm}^2$$

The corrosion rate (CR) is calculated using the relationship.

$$CR = 534W/DAT$$

where  $W$  is the weight loss (g),  $D$  is the density of metal (g/cm<sup>3</sup>),  $A$  is the total surface area of coupons (cm<sup>2</sup>), and  $T$  is the exposure time (hrs).

$$CR \text{ (Control 7 days MCS)} = 534 \times 0.030 / (7.87 \times 40.85 \times 168)$$

$$= 16.02 / 54010.24$$

$$= 2.94 \times 10^{-4} \text{ mpy}$$

$$CR \text{ (Control 7 days MS)} = 534 \times 0.042 / (7.87 \times 40.85 \times 168)$$

$$= 4.15 \times 10^{-4} \text{ mpy}$$