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Procedia Manufacturing 35 (2019) 513–521

Procedia MANUFACTURING

www.elsevier.com/locate/procedia

2nd International Conference on Sustainable Materials Processing and Manufacturing

(SMPM 2019)

The effect of a sulphate-reducing bacteria on the rate of corrosion of steel alloys

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Abstract

In this article, we investigate the effect of micro-organisms on the rate of corrosion of stainless steel and mild steel alloys. The three analytical techniques we will employ in measuring the rate of corrosion are the electrochemical impedance spectroscopy, cyclic polarization and the mass loss method. The test material used is the 316L stainless steel and the mild steel coupons. The microorganism we are going to use for this investigation is the sulphate-reducing bacteria (SRB). The scope of the study will cover the cultivation of the micro-organism, cell count, electrochemical testing, cyclic polarization testing, analysis of corrosion product, mass loss and the pitting morphology consistent with the microbiologically induced corrosion mechanism. Our results show that the chemical composition of the mild steel and stainless steel test material conformed to SAE1020 and Type 316L stainless steel respectively. We also found that the corrosion rate of mild steel in both biotic and abiotic systems was significantly higher than that of the 316L stainless steel. The biotic system was more corrosive for both the mild steel and the 316L stainless steel. The biotic system showed a substantial corrosion effect in two days while the abiotic system showed the same effect after seven days. The cell count procedure confirmed the presence of sulphate-reducing bacteria throughout the test.

Peer-review under responsibility of the organizing committee of SMPM 2019.

Keywords: Type your keywords here, separated by semicolons ;

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2351-9789
Peer-review under responsibility of the organizing committee of SMPM 2019.
10.1016/j.promfg.2019.05.073

1. Introduction

Microbiologically induced corrosion (MIC) is a complex type of environmentally assisted corrosion. It involves the deterioration of metals as a result of the metabolic activity of micro-organisms. MIC can accelerate material failure in a wide range of environments ranging from oil and water pipelines, machinery to biomedical utensils. There are different types of bacteria that play a major role in the influence of MIC and these can be categorized as either aerobic or anaerobic. Aerobic bacteria are organisms that require oxygen to be active while anaerobic bacteria do not. The process conditions determine the type of micro-organisms that can breed and thrive in that type of particular environment. Bacteria involved in MIC can also be categorized as sulphate-reducing, acid-producing, slime-forming, iron-reducing, nitrate-reducing and iron-oxidizing bacteria (Clarke & Aguilera, 2007). These bacteria may reduce the metal directly, produce corrosive metabolic by-products, or produce a biofilm that indirectly alter the local environment to promote corrosion.

MIC affects the performance of many plants in South Africa (Danha et al. 2016), due to the downtime and costs involved in repairing or replacing the corroded pipe lines, process equipment and fittings, in different types of industries. As a result, a Government funded research institute in South Africa (Mintek) realized the need to enhance its knowledge on MIC in order to effectively address issues related to this phenomena occurring in various industries.

In this article, we investigate the effect of bacteria on the rate of induced corrosion on the two alloys of steel that are most commonly used in the manufacture of industrial pipes namely, stainless steel and mild steel. We aim to determine and compare the corrosion behavior of the alloys (Dubent et al. 2010) using the electrochemical impedance spectroscopy method, cyclic polarization and the mass loss techniques. We will analyze the corrosion products formed on the surface of the materials and also propose a technique that can be employed in order to protect these alloys from this form of bio-corrosion.

2. Theoretical background

All Chemical and microbiological analysis, metal characteristics and its corrosion behavior and analysis of the products of corrosion are essential activities required in order to understand a corrosion problem (Starosvetsky et al. 2007).

Corrosion attacks as a result of MIC include pitting, de-alloying, erosion, galvanic and hydrogen embrittlement (Castleberry & Teague, 2014). Pitting corrosion caused by MIC is microscopic in nature and can only be detected with the help of a microscope (Little et al. 2007).

Cases of MIC induced pitting corrosion have been reported in various types of plants in South Africa. Hence, MIC testing should be regarded as an important part of mitigating and controlling corrosion in industry (Kearns & Little, 1994).

There are different types of mechanisms responsible MIC. According to Clarke and Aguilera (2007), many of the complex cellular interactions of bacteria are still unclear and can vary by system; there appears to be several somewhat universal steps in the MIC process. They are as follows:

1. Bacteria rapidly reproducing after colonizing and attaching themselves to metals.
2. Tubercles are formed from aerobic metabolism of the metal surface they colonized.
3. The tubercles then create micro-environments on the surface of the metal. Tubercles are hard protective shells formed by biological activity. Tubercles typically have an open interior fluid cavity over the corrosion floor area with an approximate pH of 3 to 4.
4. The under deposit area becomes oxygen depleted relative to the immediate environment.
5. Under deposit anaerobic bacteria metabolize the metallic surface and excrete acids as by-products which are very aggressive to the materials. The pH is reduced to between 2 and 4, which chemically attacks the metallic component surface.

2.1. Common techniques of evaluating microbiologically induced corrosion

There are various techniques that can be used to measure MIC. These techniques involve the use of metallurgical and microbiological, electrochemical and biotechnological analysis in order to evaluate the effect of the micro-organisms on the surface of the samples (Kearns & Little, 1994). We will limit our discussion only to the techniques we chose to use in performing our analysis.

2.1.1 The dielectric spectroscopy method

The dielectric spectroscopy method evaluates the dielectric nature of materials. The dielectric method measures corrosion through the interaction of an electrochemical field with the dipole moment of a metallic surface. The dielectric technique is a method used to measure corrosion in electrochemical systems. This technique is time consuming and requires that the system be at steady state during the period of measurement (Burleigh et al. 2001).

2.1.2 The dielectric spectroscopy method

The cyclic polarization method is usually used to measure pitting corrosion of either metals or alloys. The pitting potential of a metallic surface or sample is evaluated through a hysteresis loop. The diameter of the loop is proportional to the magnitude of pitting. The cyclic polarization method characterizes both corrosion characteristics and corrosion mechanisms (Corrosion Doctors, 2014).

2.1.3 The open circuit electrochemical potential method

The open circuit potential (OCP) method employs the difference of the potential between the working electrode and the reference electrode in a situation where no current is flowing across a cell (Maev and Leshchynsky, 2016). When a potential difference is applied to an open circuit, the system measures the open circuit potential before turning on the cell, then applies the potential relative to that measurement. (Corrosionpedia, 2014).

3. Experimental procedure

3.1. Growth of the bacteria

The sulphate-reducing bacteria was cultivated and maintained in a 3 litre fermenter with a 10% zinc acetate trap for sulphide capture (Dornberger et al. 1985). Nitrogen gas was then purged into the fermenter's head space through a sealed gas port for 15 minutes to create anaerobic conditions. The head space contains gases generated by the metabolic activity of the bacteria within the consortium. During purging, this gas is displaced into the zinc acetate trap where the hydrogen sulphide reacts with the zinc acetate to generate zinc sulphide. Table 1 shows the concentration of the feed solution required for the growth and survival of the bacterial culture.

Table 1. A recipe for the feed solution

Chemical	**Concentration (g/l)**
Ascorbic Acid	**0.1**
Sodium Chloride	**0.1**
Potassium dihydrogen Phosphate	**0.5**
Ammonium Chloride	**1.0**
Sodium Sulphate	**3.0**
Calcium Chloride Dihydrate	**0.2**

Magnesium Sulphate Heptahydrate	**2.0**
Ferrous Sulphate Heptahydrate	**0.25**
Trisodium Citrate	**0.30**
Sodium Lactate	**12.5**
Yeast Extract 6	**1.0**

3.2. Material preparation

Mild steel and stainless steel plates were purchased from a local supplier. The chemical compositions of the plates were determined using a spark emission spectroscopy. Sixteen 20mm x 10mm and four 10mm x 10mm coupons were cut from each sheet using a water cooled, automatic cut-off machine. The coupons were ground to 120 grit SiC finish. The coupons were weighed and measured to determine their weight and dimensions before testing. The 20mm x 10mm were used during mass loss coupon corrosion testing and were labelled MS1-MS16 for the mild steel and SS1-SS16 for the stainless steel. The 10mm x 10mm coupons were used for electrochemical tests. They were labelled MS1-MS4 and SS1-SS4 for the mild steel and stainless steel respectively. The coupons were cold mounted using an epoxy resin, a mixture of epofix resin and hardener and cured for 24 hours, in order to create an electrode to be used in the corrosion cell. All the glassware was autoclaved at 121°C for 20 minutes. Rubber stoppers, glass rods, graphite rods, tongs, thermometers and purges were sterilized in 70% ethanol for 24 hours followed by exposure to UV lamp for 20 minutes (Alabbas et al. 2013). The mass loss coupons were then periodically removed from the tests solutions for cell count and mass loss testing.

3.3. The mass loss procedure

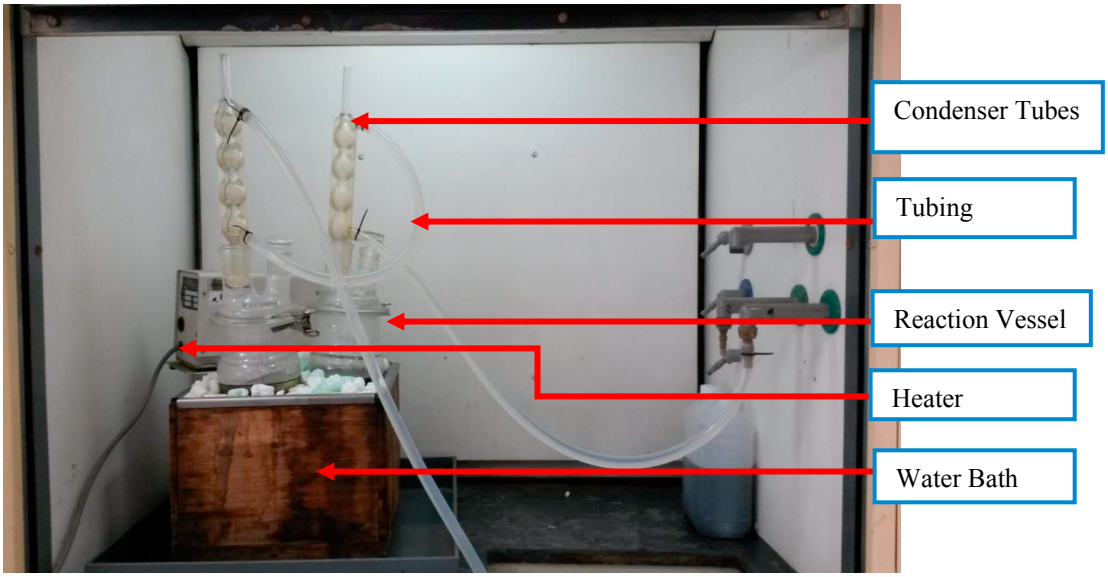

Fig. 1. Mass loss procedure experimental setup.

Four litres of feed solution were prepared by mixing distilled water with the chemicals indicated in Table 1. The pH of the solution was 5.27. Two litres of the feed solution was inoculated with 0.5 litres of a sulphur reducing bacteria consortium. Two vessels were used for the mass loss tests. One vessel was filled with two litres of the abiotic solution (control/feed solution) and the other vessel was filled with two litres of the biotic solution (SRB + feed solution). Samples labelled MS1-MS5 were placed on a sample holder and placed fully immersed in the control vessel. The samples labelled MS6-MS7 were also placed on a sample holder and fully immersed in the test media. The two vessels were purged with nitrogen gas for an hour in order to create anaerobic conditions and completely sealed before placing in a water bath filled with distilled water. The heater and the thermometer were used to maintain a testing temperature of 37°C. Condenser tubes were utilized in order to minimize any evaporation that might occur. Plastic tubes were used to maintain the flow of water, as shown in Figure1. The test was left to run for a period of 15 days. The same procedure was followed for the stainless steel coupons.

3.4. The electrochemical testing procedure

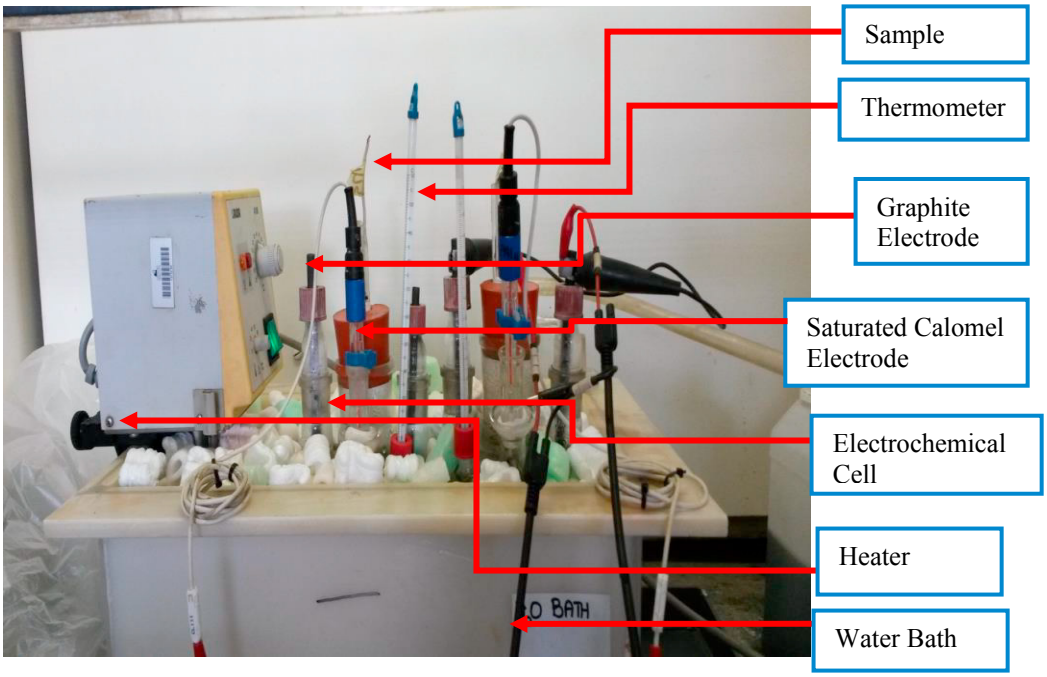

Fig. 2. The electrochemical procedure experimental setup.

Two electrode corrosion cells were used for the electrochemical test. Each cell comprised of a working electrode, two graphite rods (auxiliary electrode) and saturated calomel electrode (reference electrode) (Yin et al. 2011). One cell was filled with approximately one litre of abiotic solution and the other vessel was also filled with approximately one litre of biotic solution. Each cell was purged with nitrogen gas for an hour in order to create anaerobic conditions, and were completely sealed and placed in a water bath filled with distilled water. The heater and the thermometer were used to maintain a testing temperature of 37°C. The dielectric spectroscopy, open circuit potential (OCP) and the cyclic polarization measurements were carried out simultaneously under both biotic and abiotic conditions for a period of 15 days. We carried out the measurements in a conventional three-electrode ASTM electrochemical cell coupled with a potentiostat (Alabbas et al. 2013), as shown in Figure 2. During the electrochemical test, each cell was purged with nitrogen gas. Each day, a linear polarisation resistance scan was performed on the electrodes for 30 minutes followed by electrochemical impedance scanned from 105 to 10-2 Hz with an AC amplitude of 10mV. This was done for both abiotic and biotic cells for 15 days. On the 16th day, a

cyclic polarisation scan was performed scanning from -250mV vs the OCP at 10mV/s. The scan direction was reversed when the current reached 0.5mA/cm2. A sample of the solution was also removed from the reaction vessel for cell count in order to estimate the number of sulphate-reducing bacteria in the solution.

4. Results and discussion

4.1 Concentration of microorganisms in water

Figure 3 shows the distribution of bacteria in the solution diluted 100 times with distilled water. The population of microorganisms in diluted water demonstrates that without dilution the cultured water had a large volume fraction of sulphate-reducing bacteria. The corrosive action of bacteria on metal would be more devastating with increased population of micro-organisms infesting the water. Thus the corrosion of a particular metal by sulphate-reducing bacteria will depend on it corrosion resistance.

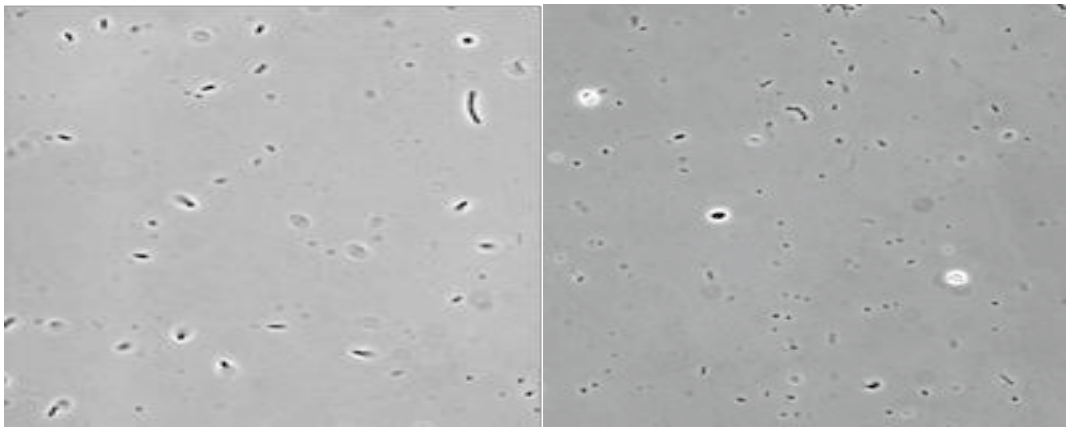

Fig. 3. Micrographs showing sulphate-reducing bacteria under optical microscope.

4.2 Mass loss and corrosion rate results

Table 2. Mass loss and corrosion rate results of mild steel

Mild steel							
Sample	**Condition**	**Area (mm^2)**	**Mass (g) before**	**Mass (g) after**	**Mass Loss (g)**	**Time (days)**	**Corrosion Rate (mm/y)**
A	**ABIOTIC**	5.54	4.5900	4.5730	0.0173	117	0.298
B		5.53	4.9500	4.9429	0.0073	189	0.078
C		5.70	6.1500	6.1301	0.0205	260	0.154
D		5.66	5.1700	5.1636	0.0065	332	0.039
E		5.69	5.5200	5.4996	0.0211	360	0.115
F	**BIOTIC**	5.51	3.7200	3.7123	0.008	117	0.138
G		5.58	4.4800	4.4713	0.0089	189	0.094
H		5.64	5.5300	5.5106	0.020	260	0.152
I		5.69	6.0800	6.0445	0.0356	332	0.210
J		5.60	4.6700	4.6486	0.0221	360	0.123

Table 2 shows that the corrosion rates of 0.3 to 0.1 mm/year were relatively low with no significant difference in the corrosion observed for the biotic and abiotic solutions indicating that the analysis was performed over a short exposure period and that longer exposure times would show corrosive effect of organisms in water on mild steel.

3.5. The mass loss procedure

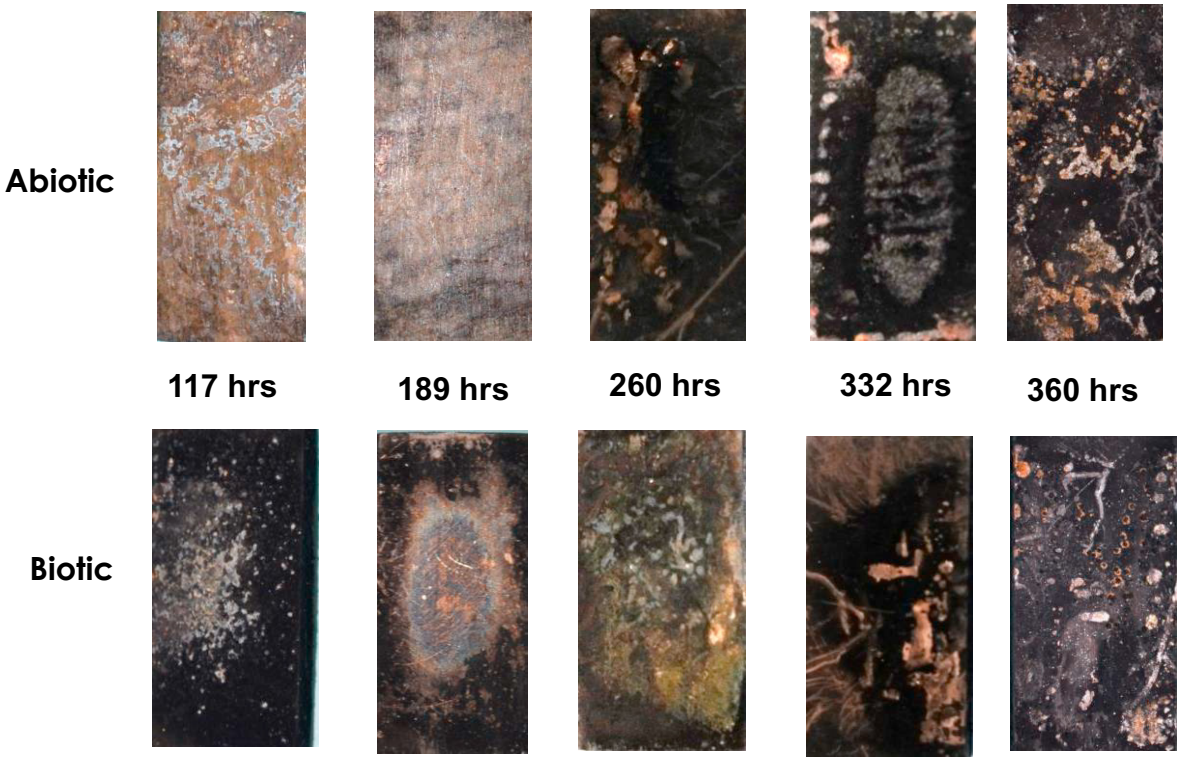

Fig. 4. Corrosion on mild steel samples exposed to biotic and abiotic solutions.

The corrosion stains on the mild steel samples exposed to biotic and abiotic solutions (Krun et al. 2003) do show some difference. This shows that the corrosion that occurred in this investigation can be attributed to a sulphate-reducing bacteria. A longer exposure period would have made the difference even more pronounced. As expected the corrosion of stainless steel under the same conditions was considerably lower as evident in Figure 5. There is very little corrosion if any on stainless steel samples soaked in biotic and abiotic solutions.

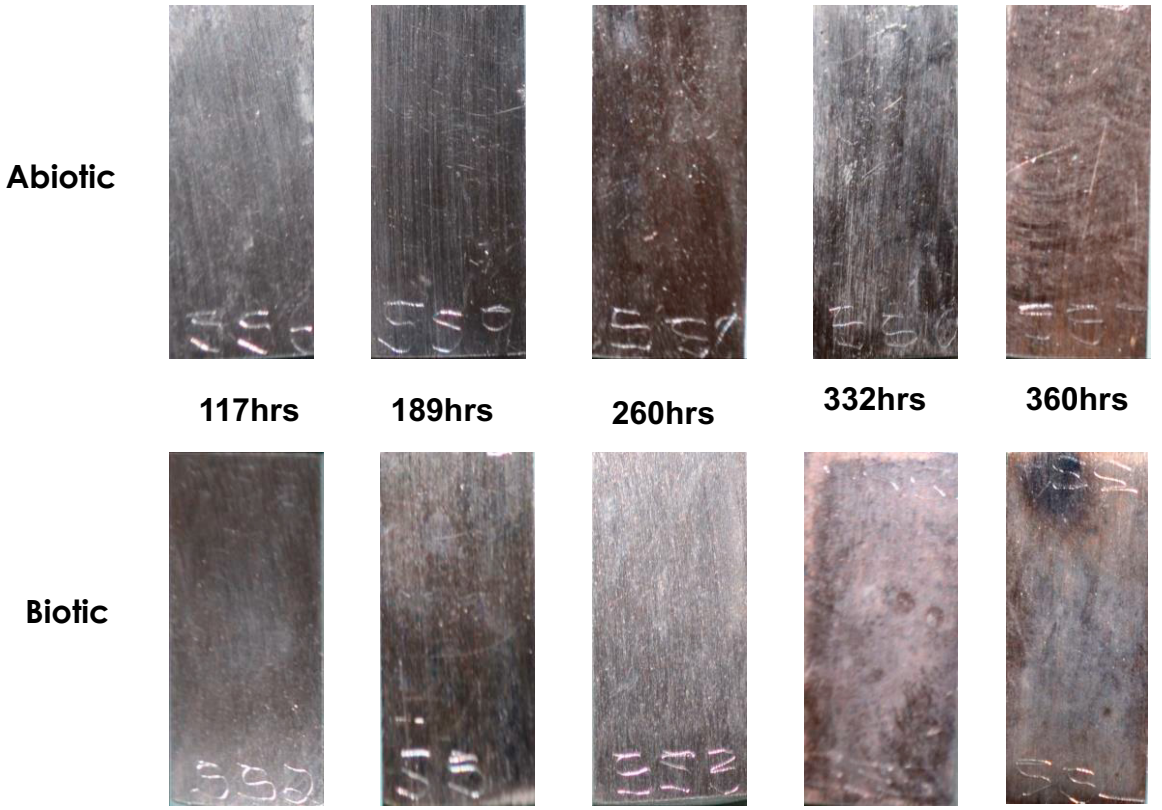

Fig. 5. Surface of stainless steel samples exposed in biotic and abiotic solution

5. Conclusion

According to theoretical constructs, the sulphate-reducing bacteria have a corrosive effect on metals particularly those with low corrosion resistance such as mild steel. The investigation carried out in the limitation of time shows that corrosion due to bacteria occurred to an observable extent in the 360 hours of exposure to biotic and abiotic solutions. This fact is confirmed by the difference in corrosion caused by the two solutions. Thus the corrosion on the samples can be attributed to the sulphate-reducing bacteria. However, we recommend that similar experiments should be run for even longer periods of exposure to water containing sulphate-induced bacteria surviving on natural nutrients in order to eliminate the effect of artificial nutrients for bacteria, which also have corrosion effects. Results of such experiments would assist in material selection for pumps and pipes for waste water systems.

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