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Effects of *Desulfotomaculum* sp on corrosion behaviour of mild steel and aluminium in sea water

ABSTRACT

The microbiologically influenced corrosion of mild steel and aluminum in sea water (SW) caused by a sulfate reducing bacterium (SRB), *Desulfotomaculum* sp was investigated. The corrosion rates were evaluated at intervals of ten days for a period of sixty days using gravimetric and electrochemical methods. Results showed that corrosion rate decreased with exposure time after initial increase. The plot of the electrode potential (EP) with the exposure time shows a decrease as resistance increased due to the corrosion product formed on the surface of the metals. Aluminum recorded a maximal EP reduction (-0.85 mV) after 60 days of incubation, with an onset potential of -0.53 mV after 10 days. The more negative the EP, the greater the tendency to form ions and hence to corrode. The average corrosion rate of mild steel and aluminum coupons in the presence of SRB was 4-fold higher compared to coupons on media without *Desulfotomaculum* sp.

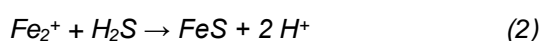
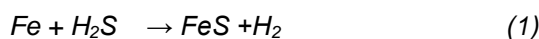
Keywords: Microbiologically influenced corrosion, Corrosion rate, Electrode potential, SRB, Passivity, Metal

1. INTRODUCTION

Many forms of microbiologically influenced corrosion (MIC) under non flowing water body are understood, however, there is still some uncertainties regarding MIC under fluid flow conditions [1, 2]. Recent studies showed that in stagnant and low velocity conditions, the diffusion of nutrients from the environment to the biofilm was limited, while at high velocities nutrients were replenished in the bacterial biofilm resulting in higher ATP concentrations and higher corrosion rates [2].

Sulfate-reducing bacteria (SRB) carry out dissimilatory reduction of sulfate to H₂S [3]. They grow well in anaerobic environment, such as soil sediments, oil fields and wastewater treatment plants. Metal and their alloys corrode easily in anaerobic environments [4]. In Nigeria for example and in many other nations of the world, many oil and gas pipeline pass through both sea and fresh water bodies. Pipelines, offshore oil platforms and underground structures have been reported to be

vulnerable to biological corrosion which is assumed to be mediated by different groups of microorganisms respiring with oxidized compounds such as sulfate, nitrate, ferric iron or carbon dioxide. Microbial influenced corrosion caused by SRB is a major cause of corrosion causing about \$30 -40 billion in United States alone [5]. Studies have shown that the corrosion rate of steel increased six times in the presence of SRB compared with that of sterile solution [6]. The mechanism by which sulfate reducers accelerate metal corrosion include the formation of the biofilms, which affect the electrochemical characteristics of the metal surfaces, bound metal ions and the corrosion products, such as iron sulfides [7] and by altering the chemistry at the interface between the metal and the bulk fluid [8,9]. The corrosiveness of these organisms is partly due to their metabolic product H₂S and partly due to a supposed more direct electrochemical effect termed cathodic depolarization. Hydrogen sulfide H₂S accelerates metal corrosion by acting as a source of bound protons and by precipitation of Fe²⁺ as FeS.



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The H₂ form from the above reaction may be utilized further by SRB or by other H₂⁻ scavenging microorganisms. The factors controlling anaerobic SRB corrosion are: the utilization of hydrogen by sulfate-reducing bacteria, cathodic depolarization by precipitated ferrous sulfide, the prevention of formation of protective sulfide film in the presence of excess ferrous ions, anodic stimulation by the sulfide ions and the formation of local concentration of cells.

SRB are capable of causing severe corrosion of iron materials in water system because they produce enzymes which have the power to accelerate the reduction of sulfate compounds to corrosive hydrogen sulfide, thus SRB acts like a catalyst in the reduction reaction [10]. SRB occur naturally in surface of waters including sea water. Author reported that Sulfate reducing bacterium *Desulfovibrio vulgaris* caused severe microbiologically influenced corrosion of zinc and galvanized steel [11]. Author studied the effects of sulfate reducing bacteria on corrosion of carbon steel Q235 in soil-extract solution [12].

Most offshore rigs, pipe lines and metal wears pass through and mostly in direct contact with sea water. It is therefore important to study the effects SW environment can have on the long-time integrity and corrosion behaviour of a metal. *Desulfotomaculum* sp are usually found in underground water, inside sediments or rock or feces of animals where little oxygen are available. Their presence can be identified by the release of hydrogen sulfide gas with its rotten egg smell. However, unlike some species of SRB, very little is known about the corrosion behaviour of *Desulfotomaculum* species on metals on sea water

environment [3]. Studied the corrosion behavior of low-alloy steel in the presence of *Desulfotomaculum* sp using Tafel polarization test, mass loss method and electrochemical impedance spectroscopy (EIS). They observed that the corrosion current reached its maximum value 14 hours after incubation and decreased afterwards due to increase in accumulation of corrosion products. In the present study, the effect of *Desulfotomaculum* sp on the corrosion behaviour of mild steel and aluminium widely used in construction and petroleum industry was investigated in SW using mass loss and the electrochemical methods.

2. MATERIALS AND METHODS

The strain of SRB used in this study was isolated from a corroding oil tank in an oil depot. The composition of the medium used the enrichment and cultivation of the SRB was: API RP-38 medium (g/L), containing MgSO₄·7H₂O 0.2; ascorbic acid 1.0, NaCl 10.0, KH₂PO₄ 0.5, Sodium lactate 4.0, Yeast extract 1.0, Fe (NH₄)₂(SO₄)₂ 0.02 [12]. Incubation was done anaerobically. The isolate is spore-forming, spherical, motile and gram-negative bacteria. It grows optimally at 30–32 °C and pH 6.8–7.2. The cells are curved rods shaped [13]. The organism isolated physiologically resembles *Desulfotomaculum* sp. The stock culture was maintained in a medium under nitrogen atmosphere at 4 °C.

The mild steel and aluminium used in this study was obtained from the material and metallurgical department of the University. The composition is as follows (table 1).

Table 1. Chemical composition of the steel

Tabela 1. Hemijski sastav čelika

Steel Grade	C	Si	Cu	Mn	P	Cr	Ni	Sn	S	Fe
MS (wt %)	0.18	0.23	0.20	0.80	0.03	0.05	0.55	0.02	0.04	Bal.
Al(>99.5%)										

Key: MS= Mild steel; Al=Aluminium

The mild steel coupons were cut from raw metal sheet to smaller size of 2 x 2 x 2cm for the gravimetric corrosion measurements. The coupons were polished with 400-1000-grit emery paper, rinsed with double-distilled water, degreased with acetone and then air-dried. The total areas and initial weight of the coupons were determined before the corrosion tests. This is because two

coupons may be identical in shape and surface area but different in weight.

The SW used was collected from offshore base in Port Harcourt, Rivers State Nigeria. The analysis of the water composition is in Table 2. The SW was autoclaved at 121 °C for 20 mins and stored at 4 °C before use.

Table 2. Chemical composition of the sea water

Tabela 2. Hemijski sastav morske vode

Chemical composition	O ₂	H ₂	Cl	Na	Mg	S	Ca	K	Br	Ca	Br	B	F
Molar mass (g/mol)	15.9	1.0	35.4	22.9	24.9	32.0	40.0	39.0	79.9	40.0	79.9	10.8	18.9

Corrosion test

The test coupons were placed in N₂ flushed glass tubes [3] suspended with a cotton thread which passes through the hole in each coupon and sterilized by autoclaving. Thereafter, 20mL of sterile sea water was added and the medium was inoculated with a 24 h grown standardized culture with a concentration of 120cell/mL. The entire experiments were uniformly prepared in duplicate on the same day. At 10 days interval two coupons from a tube are taken out, cleaned and weighed and the average of three values was taken. This is meant to observe the stage-by-stage progress of corrosion based on metal loss over time as well as to ensure the consistency of the weight loss and corrosion rate results. The value of the weight loss and corrosion rate based on weight loss was calculated from the equations (3) and (4) respectively:

$$\Delta W = W_o - W_i \quad (3)$$

$$CR = \frac{k\Delta W}{A\rho t} \quad (4)$$

A=Exposed surface area =2(LW+LH+HW) cm², where L= length of the coupon, W= width of the coupon, H= height of the coupon or thickness, k = corrosion rate constant (143,700 mpy), ρ =density of metal coupon (g/cm³), W_o = initial weight, W_i = final weight, ΔW=weight loss of coupon (g); t = time (days).

The electrochemical corrosion study was conducted using a multi meter on each of the metal coupons exposed to the bacteria in SW and control respectively with saturated calomel electrode (SCE) as reference electrode.

3. RESULTS

The corrosion rate of MS and Al coupons without the bacteria and with *Desulfotomaculum* sp was calculated from equation 4 and are shown in Tables 3 and 4. The mean corrosion rates at the end of the 60 days incubation was (14.64mpy for MS and 15.25mpy for Al respectively) which was four times higher when compare with the control (3.88mpy for MS and 4.23mpy for Al respectively).

Table 3: Average weight loss (g) and corrosion rate of mild steel after exposure to *Desulfotomaculum* sp in sea water

Tabela 3. Prosečan gubitak težine (g) i stopa korozije mekog čelika nakon izlaganja *Desulfotomaculum* sp u morskoj vodi

Coupon	Exposure time (d)	Density (gcm ⁻³)	Surface area (cm ²)	ΔW Control (g)	ΔW (g)	CR (control), (mpy)	CR (mpy)
M1	10	7.85	12	0.059	0.046	0.92	5.25
M2	20	7.85	12	0.085	0.038	0.65	2.16
M3	30	7.85	12	0.011	0.050	0.58	1.90
M4	40	7.85	12	0.024	0.103	0.92	2.93
M5	50	7.85	12	0.016	0.061	0.51	1.39
M6	60	7.85	12	0.012	0.053	0.30	1.01

Table 4: Average weight loss (g) and corrosion rate of aluminium after exposure to *Desulfotomaculum* sp in sea water

Tabela 4. Prosečan gubitak težine (g) i stopa korozije aluminijuma nakon izlaganja *Desulfotomaculum* sp u morskoj vodi

Coupon	Exposure time (d)	Density (gcm ⁻³)	Surface area (cm ²)	ΔW Control, (g)	ΔW (g)	CR (Control), (mpy)	CR (mpy)
L1	10	2.70	12	0.0034	0.026	1.51	8.62
L2	20	2.70	12	0.0024	0.006	0.55	0.99
L3	30	2.70	12	0.0045	0.001	0.68	0.11
L4	40	2.70	12	0.0041	0.048	0.46	3.98
L5	50	2.70	12	0.0058	0.006	0.52	0.39
L6	60	2.70	12	0.0058	0.021	0.52	1.16

4. DISCUSSION

It was observed (Figure 1 and 2) that corrosion rate of mild steel and aluminium decreased with exposure times. This experimentally observed

behaviour was due to the formation of an impermeable protective oxide film on the surface of the metals (Table 1). In this state, the steel is said to be passive and does not corrode easily [14,15].

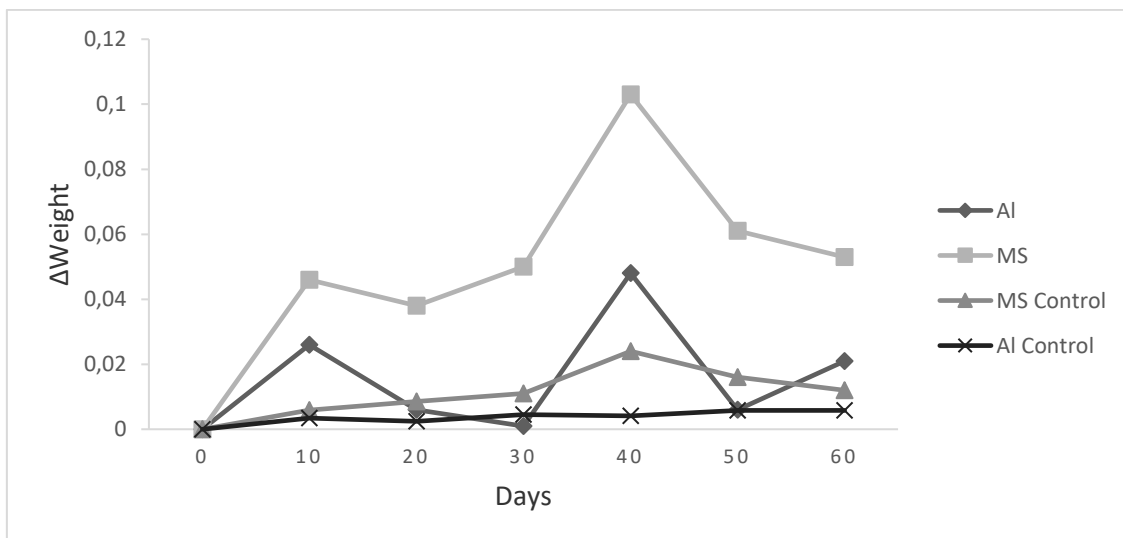


Figure 1. Gravimetric data of mild steel and aluminium in sea water in the presence of *Desulfotomaculum* sp

Slika 1. Gravimetrijski podaci mekog čelika i aluminijuma u morskoj vodi u prisustvu *Desulfotomaculum* sp

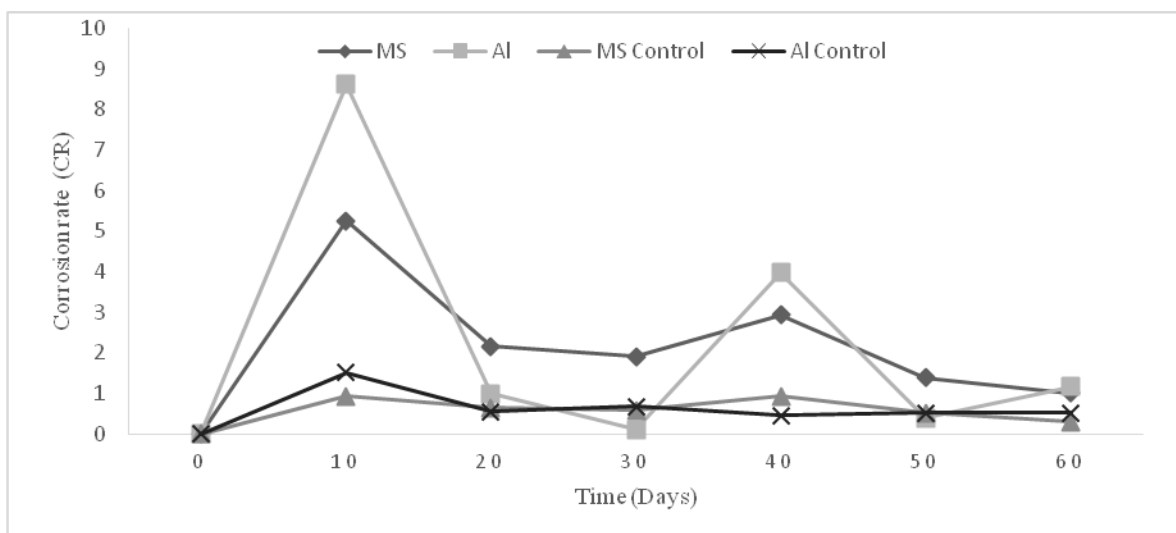


Figure 2. Corrosion rate of mild steel and aluminium in sea water in the presence of *Desulfotomaculum* sp

Slika 2. Brzina korozije mekog čelika i aluminijuma u morskoj vodi u prisustvu *Desulfotomaculum* sp

Tables 3 and 4 showed that weight losses of both mild steel and aluminium exposed to *Desulfotomaculum* sp were greater than the losses observed when the metals were not exposed to the organism. It is therefore possible that the loss in weight might have been caused by the bacteria. The increased in corrosion rate observed in first 10 days of incubation could also be due to high rate of permeability of corrosion inducing agents such as OH^- and SO_4^{2-} . SRB are able to accelerate the reduction of sulphate compounds to corrosive hydrogen sulphide. After the 10th day, the aggressive ions in the environment could not be absorbed by the protective oxide film formed by the

actions of the SRB. This led to the decrease in corrosion rate with higher exposure times except for the slight increase observed after the 40th day [16], also observed a similar increase in corrosion rate in the first 10 days of incubation of mild steel with SRB. Studies have shown that 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 such as oxides, sulphates, carbonates or nitrides [14]. If these products are not removed from the surface of the steel, the rate of corrosion will slow down. The duration taken by the corrosion inducing agents to diffuse through the oxide corrosion products to the

metals, (the base metal) may have contributed significantly to the observed difference in the corrosion rates. These corroborates the findings of [14, 17,18].

The decrease in pH after sixty days of incubation followed a higher corrosion rate and weight loss (Table 5 and Figure 3).

Table 5. Average pH readings for mild steel immersed in fresh water in the presence of *Desulfotomaculum* sp

Tabela 5. Prosečna pH vrednost za meki čelik uronjen u slatku vodu u prisustvu *Desulfotomaculum* sp

Days	Day 0	Day 10	Day 20	Day 30	Day 40	Day 50	Day 60
pH	6.80	3.80	4.20	5.70	4.30	4.60	4.70
	6.80	3.60	4.80	4.80	4.40	4.90	5.10

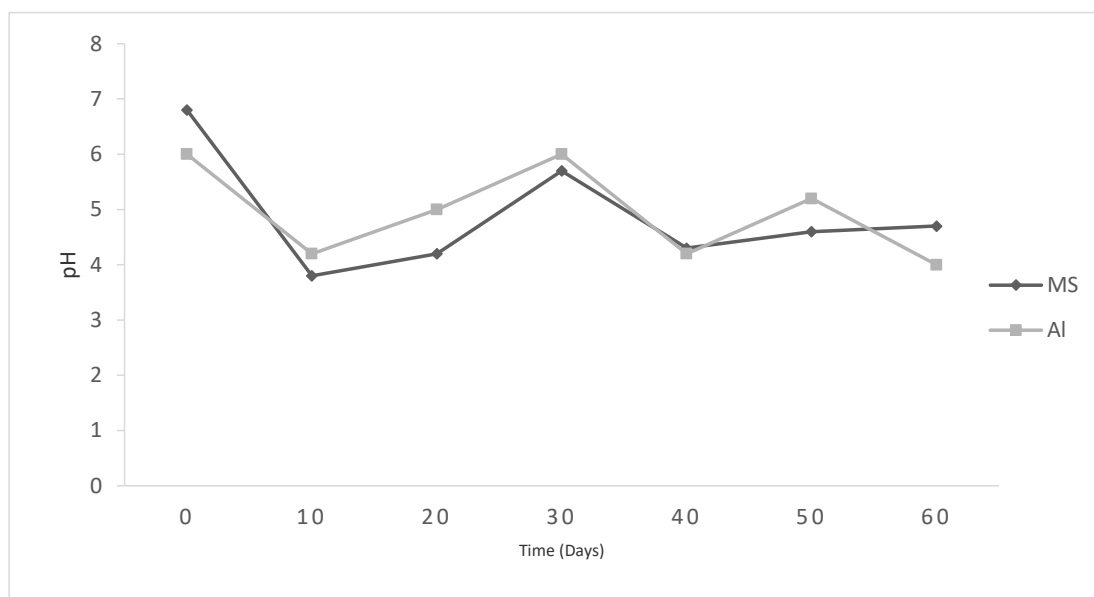


Figure 3: Variation of pH with exposure time in (days) for mild steel and aluminium in the presence of *Desulfotomaculum* sp

Slika 3. Varijacija pH sa vremenom izlaganja u (danima) za meki čelik i aluminijum u prisustvu *Desulfotomaculum* sp

A careful study of the pH variation with exposure time shows that the corrosion rate and weight loss increased with decrease in pH [19, 20]. Previous studies by [21] showed that pH above 7.2 reduced the adhesion of corrosion products and therefore enhanced corrosion. It therefore suggests that the passivity of metals decreases as the pH increases. Recent studies have found that in order to survive and grow in high alkaline or acidic environment, SRB develops several strategies to combat the environmental challenges which include maintaining pH homeostasis in their cytoplasm and adjusting metabolic activities. SRB can regulate environmental pH because of their metabolism [2]. The potential capacity of pH regulation by SRB have important consequences for electrochemical aspect of biocorrosion

processes. In their study on the effect of pH regulation by sulfate-reducing bacteria on corrosion behaviour of duplex stainless steel in acidic artificial seawater (Table 2) [2], observed that the results for the first was driven by pH in solution rather than by bacteria. However they further observed that increasing pH during the course of the experiment slowed down the corrosion process.

Rate of corrosion is proportional to the rate of electron transferred between electrode and electrolyte. The plot of the electrode potential with the exposure time (Figure 4) shows that the EP (voltage) decreased as resistance increased due to the corrosion product formed on the surface of the metals [22]. This further shows that the lower the potential, the higher the corrosion.

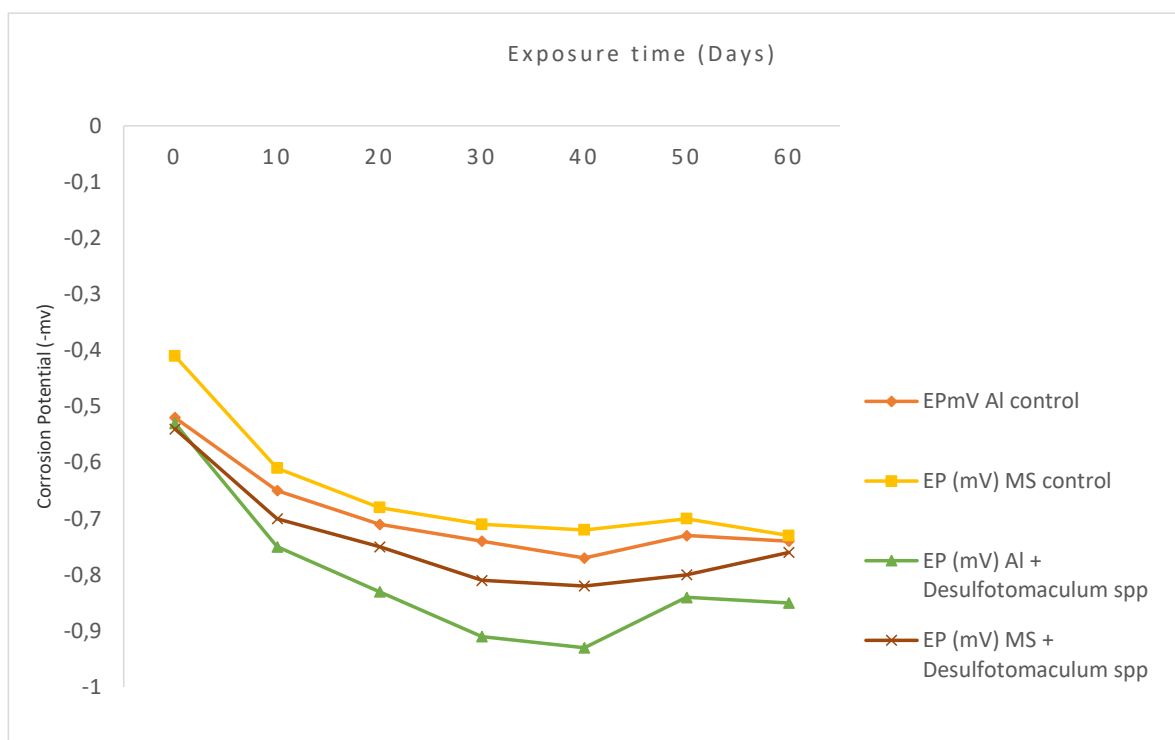


Figure 4: Variation of Potential (-mV) with exposure time (days) for mild steel and aluminium exposed to *Desulfotomaculum* sp and control in sea water

Keys: EP=Electrode potential, MS=Mild steel, Al=Aluminium, mV=mini volt

Slika 4. Varijacija potencijala (-mV) sa vremenom izlaganja (dani) za blagi čelik i aluminijum izloženi *Desulfotomaculum* sp i kontrola u morskoj vodi

EP=Potencijal elektrode, MS=Meki čelik, Al=Aluminijum, mV=mini volt

Table 6. Corrosion potential of Mild steel and aluminium in the presence of *Desulfotomaculum* sp in sea water

Tabela 6. Potencijal korozije blagog čelika i aluminijuma u prisustvu *Desulfotomaculum* sp u morskoj vodi.

	0 Days	10 Days	20 Days	30 Days	40 Days	50 Days	60 Days
	EP (mV)	EP (mV)	EP (mV)	EP (mV)	EP (mV)	EP (mV)	EP (mV)
MS (Control)	-0.41	-0.61	-0.68	-0.71	-0.72	-0.70	-0.73
Al (Control)	-0.52	-0.65	-0.71	-0.74	-0.77	-0.73	-0.74
MS+ <i>Desulfotomaculum</i> sp	-0.54	-0.70	-0.75	-0.81	-0.82	-0.80	-0.76
Al + <i>Desulfotomaculum</i> sp	-0.53	-0.75	-0.83	-0.91	-0.93	-0.84	-0.85

In Table 6, Al recorded the highest decrease in EP (-0.85mV) on the 60th day of the study. It had initial potential of -0.53mV. This decrease in EP shows an increase in corrosion rate which also corresponds with the increase in weight loss recorded in the gravimetric study. However, there was a sharp increase in EP from 30th day (-0.81mV) to 40th day (-0.82) for MS and -0.91mV to -0.93mV for Al showing a decrease in corrosion

rate. The more negative the EP, the greater the tendency to form ions and hence to corrode.

The observed increase in EP after 60 days of the study for both MS and Al (Figure 4) in the presence of *Desulfotomaculum* sp was also attributed to the concept of passivity caused by the formation of oxide film on the surface of the metal coupons. This resulted in the slowing down of the metal dissolution with resultant decrease in corrosion rate. The slowdown of corrosion after 10

days of incubation can also be due to the biofilm formation observed on the surface of the metals. This may have accelerated the cathodic depolarization process of the metals while also slowing down the anodic process [3]. In line with similar studies, it was observed that the EP reached its maximum value after 10 days of incubation and subsequently decreased afterwards.

5. CONCLUSION

Desulfotomaculum sp influenced the corrosion behaviour of mild steel and aluminium in SW under laboratory conditions. The incubation of the SRB with the metals were shown to affect the weight loss, corrosion rate and electrode potential of the metals within the first ten days of exposure. It was observed that the bacteria accelerated the cathodic depolarization of the metals while slowing down the anodic process as a result of corrosion products (mostly iron sulfide) and biofilm formation on the metal surfaces. The result obtained from this study support our hypothesis that *Desulfotomaculum* sp can affect the corrosion behaviour of mild steel and aluminium in SW.

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IZVOD

Efekti *desulfotomaculum* sp na korozijsko ponašanje mekog čelika i aluminijuma u morskoj vodi

Mikrobiološki uticaj na koroziju mekog čelika i aluminijuma u morskoj vodi (SV) prouzrokovane bakterijom za smanjenje sulfata (SRB), istražena je Desulfotomaculum SP. Stope korozije procenjene su u intervalima od deset dana u periodu od šezdeset dana koristeći gravimetrijske i elektrohemijske metode. Rezultati su pokazali da se stopa korozije smanjila sa vremenom izlaganja nakon početnog povećanja. Plot potencijala elektroda (EP) sa vremenom izloženosti prikazuje smanjenje kao otpor porastao zbog korozije koji se formira na površini metala. Aluminijum je zabeležio maksimalnu redukciju EP (-0,85 MV) nakon 60 dana inkubacije, sa početnim potencijalom od -0,53 mV nakon 10 dana. Što je više negativnije, to je veća tendencija da formiraju jone i samim tim da korodiraju. Prosečna stopa korozije mekog čelika i aluminijuma u medijima u prisustvu SRB-a bila je 4-puta više u poređenju na medije bez Desulfotomaculum Sp.

Ključne reči: mikrobiološki uticaja na koroziju, stopu korozije, potencijal elektroda, SRB, pasivnost, metal

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