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Open Circuit Potential Study of Stainless Steel in Environment Containing Marine Sulphate-Reducing Bacteria

(Kajian Keupayaan Litar Terbuka Terhadap Keluli Tahan Karat dalam Persekitaran yang Mengandungi Bakteria Penurun-Sulfat Marin)

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ABSTRACT

The corrosion potential of AISI 304 stainless steel coupons influenced by sulphate-reducing bacteria (SRB) has been studied. Pure colony of SRB was isolated from the Malaysia Marine and Heavy Engineering, Pasir Gudang, Johor. Open circuit potential measurements were carried out in variable types of culturing solutions with SRB1, SRB2, combination of SRB1 & SRB2 and without SRBs inoculated. The results showed that the corrosion potential, E_{oc} *increased in the presence of SRBs (in pure and mixed culture) compared to that of control. EDS analysis showed the strong peak of sulphur in coupon containing SRB cultures compared to the control. Environment Scanning Electron Microscope (ESEM) data showed that the high density cell of SRBs were associated with corroding sections of surface steel comparing with non-corroding sections for coupons immersed in VMNI medium containing SRBs.*

Keywords: Open circuit potential; stainless steel; sulphate-reducing bacteria

ABSTRAK

Keupayaan kakisan kupon keluli kalis karat bersiri 304 yang dipengaruhi oleh bakteria penurun-sulfat (SRB) telah dikaji. Koloni tulen SRB telah dipencilkan dari Kejuruteraan Berat dan Marin Malaysia, Pasir Gudang Johor. Pengukuran keupayaan litar terbuka telah dijalankan dalam berbagai-bagai jenis larutan pengkulturan menggunakan SRB1, SRB2, kombinasi SRB1 dan SRB2 serta larutan tanpa kultur SRB. Keputusan menunjukkan keupayaan kakisan, E_{oc} *meningkat dengan kehadiran SRB (dalam kultur tulen dan gabungan kultur) berbanding kawalan. Analisis EDS menunjukkan puncak sulfur yang tinggi dalam kupon yang mengandungi kultur SRB berbanding kawalan. Data dari mikroskop elektron imbasan sekitaran (ESEM) menunjukkan kepadatan sel SRB yang tinggi berasosiasi di bahagian permukaan keluli yang karat berbanding bahagian yang tidak berkarat bagi kupon yang direndam dalam larutan VMNI yang mengandungi SRB.*

Kata kunci: Bakteria penurun-sulfat; keluli kalis karat; keupayaan litar terbuka

INTRODUCTION

Microbiologically influenced corrosion (MIC) is undoubtedly a phenomenon of great importance in marine corrosion processes. The anaerobic corrosion of steel induced by the sulphate-reducing bacteria (SRB) is of particular interest, both economically and scientifically.

The bulk of the literature on MIC detailed the anaerobic corrosion of mild steel, caused by the SRB and characterized by the presence of black iron sulphide. The action of the SRB is not limited to mild steel and has been reported for copper and its alloys and stainless steel (Angell et al. 1995; Sarioglu et al. 1997).

Open circuit corrosion potential measurements have been used in MIC studies for many years. It has been often reported that the microbial films changed the corrosion potential or the open circuit corrosion potential of passive metals that immersed in natural seawater (Johnsen & Bardal 1985; Scotto et al. 1985; Dexter & Gao 1988; Scotto 1989; Angell et al. 1995; Werner et al. 1998; Angell & Urbanic 2000). Corrosion potential or OCP variation with time can be measured by determining the voltage difference between a metal immersed in a liquid medium and an appropriate reference electrode (generally, the standard calomel electrode) (Scotto et al. 1985; Dexter & Gao 1988; Videla 1991). Measurement of OCP changing with time is important for estimating the effect of depolarizers on corrosion reactions. A plot of potential as a function of time could be useful to detect the initiation or an accelerated attack of SRB (Tuovinen & Cragnolino 1986). An increase of OCP means depolarization of cathode and increase corrosion, a drop in potential is evidence for decreased corrosion. Also rapid changes in the corrosion potential can be used to indicate a depolarization or enhancement of the anodic reaction, or to the formation of a semiprotective film (Little et al. 1997).

The role of SRB in corrosion of stainless steel coupons has been studied using open-circuit potential for measurements the change of corrosion potentials. Surface

characterization and composition of the corrosion products were determined by ESEM and energy dispersive analysis x-ray (EDAX).

MATERIALS AND EXPERIMENTAL

CULTURAL CONDITIONS

The SRBs used in this work was isolated from the Malaysia Marine and Heavy Engineering (MMHE) harbours, Pasir Gudang. The collected samples were inoculated in a selective medium, following the recommendations for SRB sampling. The microorganisms were maintained in the laboratory using the VMNI medium (Table 1) proposed by Zinkevich et al. (1996) which was modified from Posgate's Marine medium C. The medium was degassed under N_2 for 30 minutes to create anaerobic condition and pH was adjusted to 7.2 using 1.0M NaOH before autoclaving at 121ºC. It was left to cool to room temperature before being inoculated with the SRBs.

The bacterial cells were spun in 30 ml centrifuge tubes for 10 minutes at 1200 rpm, the supernatant was removed and the samples were ready to be used or stored in the freezer until needed.

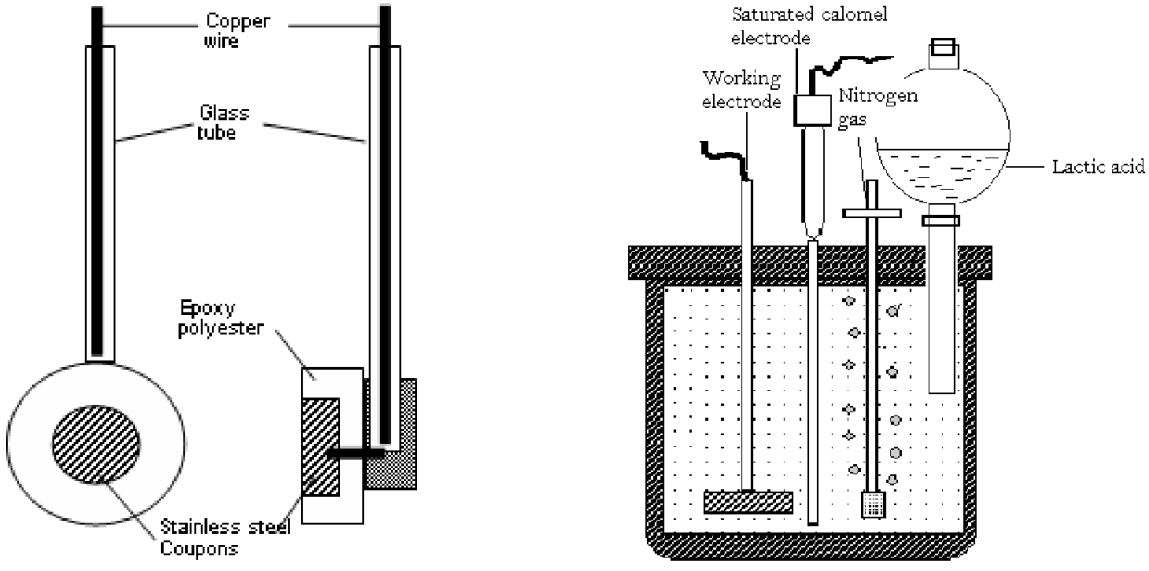
OPEN CIRCUIT POTENTIAL MEASUREMENTS

Open-circuit potential, E_{corr} changes were measured against a standard saturated calomel electrode placed in the same compartment and a schematic drawing describes the experimental situation in this case (Figure 1) and measured using a multimeter (Model Megger M8013). The stainless steel samples (as a working electrode) were immersed in the electrolyte solution exposing a circular area of about 0.708 cm^2. A copper wire was soldered at the rear of the electrode which was housed in a glass tube to protect it from the test medium. Electrochemical cell system was performed according to ASTM standard (ASTM Designation G3-89, 1999). The potential of the stainless steel electrode immersed in various conditions: (1) VMNI (control); (2) VMNI + SRB1; (3) VMNI + SRB2 and (4) VMNI + SRB1 + SRB2 were measured.

The electrolyte used was about 300ml VMNI medium and incubated at 37ºC under anaerobic condition for 15 days and during this time, several measurements were carried out daily. Results were obtained at least in triplicate. Nitrogen gas was bubbled continuously to remove all the oxygen and to maintain anaerobic conditions. To characterize and identify the corrosion products, the electrode used in potential change studies

TABLE 1. Composition of the VMNI medium

Chemical Reagents	Composition (g/L)
KH_2PO_4	0.5
NH_4Cl	1.0
$NaSO_4$	4.5
Sodium citrate	0.3
$CaCl_2.6H_2O$	0.04
$MgSO_4.7H_2O$	0.06
Casamino acids	2.0
Tryptone	2.0
Lactate	6.0
Ascorbic acids	0.1
Thioglycollic acid	0.1
$FeSO_4.7H_2O$	0.5
Trace elements (stock solution)	1.0ml
Vitamins (stock solution)	2.0ml



(a) (b)

FIGURE 1. (a) Schematic diagram of stainless steel concentric electrode (as a working electrode) and (b) sketch of the electrochemical cell

was analyzed by ESEM and Energy Dispersive Analysis X-ray (EDAX).

RESULTS AND DISCUSSION

Results of open-circuit corrosion potential, E_{oc} were measured against a standard saturated calomel electrode in the culture solution (VMNI medium) and filter-sterilize seawater are shown in Figure 2. In both sterile medium, no significant changes occurred in OCP. However in term of corrosion potentials, it is obvious that the filter-sterilized seawater was more positive values starting at – 341 mV_{SCE} and slightly increase to a constant value of about – 330mV_{SCE} while the starting potential of VMNI (control) was the lowest (– 415 mV_{SCE}) and decreased to a constant value of about – 427 mV_{SCE}.

Significantly higher corrosion potential was recorded in the filter-sterilized seawater compared to VMNI medium. The presence of the yeast extract in VMNI medium may explain the decrease in the corrosion potential observed over long periods of exposure. According to Dupont et al. (1998), yeast extract may be adsorbed on the electrode surface inhibiting the corrosion of stainless steel. More further, VMNI medium was also enriched with more organic nutrients, which is increased the complexity of the electrolyte systems.

Figure 3 shows the variations of the OCP with time for stainless steel in VMNI medium inoculated with different SRBs at 37ºC. In sterile VMNI (control), no significant changes in OCP was observed. In the presence of pure colony SRB1 (SSVSRB1), the OCP of stainless steel was ennobled (shifted in the electropositive direction) by about + 105 mV_{SCE} (from – 481 to – 376 mV_{SCE}). The starting value of SSVSRB2 was the highest (about –309 mV_{SCE}) and decreased suddenly to– 432 mV_{SCE} before increasing slowly to –353 mV_{SCE} after 11 days of exposure. E_{oc} then decreased slowly to – 408 mV_{SCE} after day 15.

When bacteria exist in the solution, the corrosion potential shifted in the opposite direction and ennoblement of stainless steel was observed, in agreement with other findings (Mansfield & Little 1990; Rainha & Fonseca 1997; Fonseca et al. 1997; Keresztes et al. 1997; Sarioglu et al. 1997). The changes of electropositive direction in the presence of SRBs case, indicate a looser passive layer compared that to the one without the bacteria. The presence of SRB especially on a metal surface often leads to highly

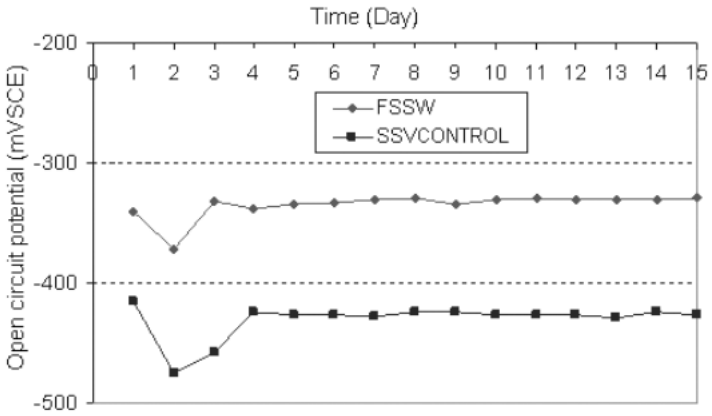


FIGURE 2. Plots of open circuit potential E_{oc} as a function of immersion time for stainless steel in VMNI medium sterile and filter-sterilized seawater

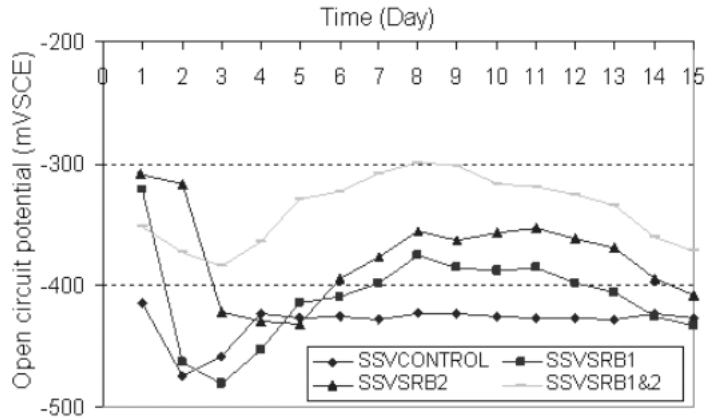
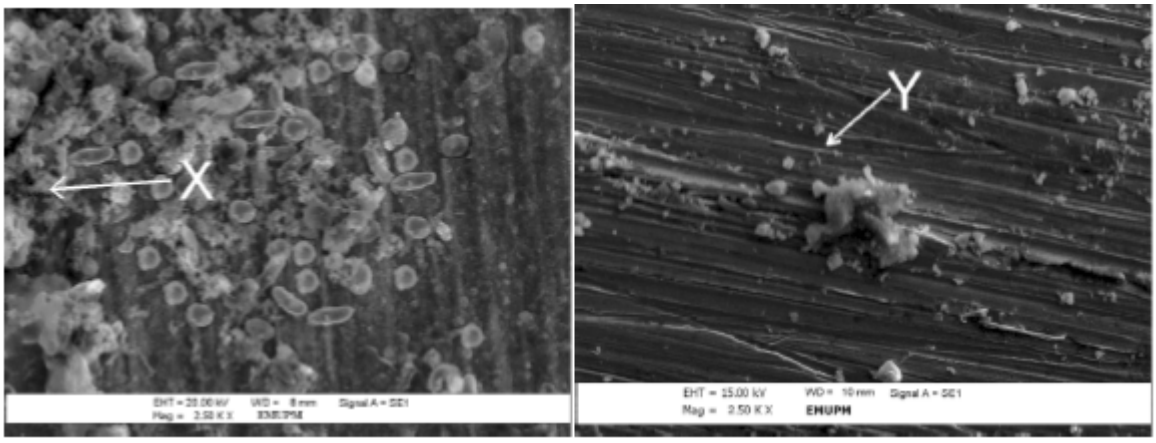


FIGURE 3. Open circuit potential for stainless steel in sterile VMNI (control) and VMNI with varies of SRB isolates

corrosion potential changes, pH and oxygen level (Costerton et al. 1995; Dexter 1995). The ennoblement of the potential in the system which presence of SRBs are indicative of the onset of localized corrosion, i.e. pitting, due to the local rupture and/or transpassive dissolution of the passive film (Fonseca et al. 1997). Videla (1996) also found pitting attack in passive films formed under active biofilm. Sudden changes in the active of positive directions were interpreted as the initiation of accelerated attack due to bacteria. This agrees with alternative mechanisms where not only the bacteria but also other probable corrodants like sulphide are thought to be effective on corrosion (Dexter et al. 1991; Pope & Morris 1995).

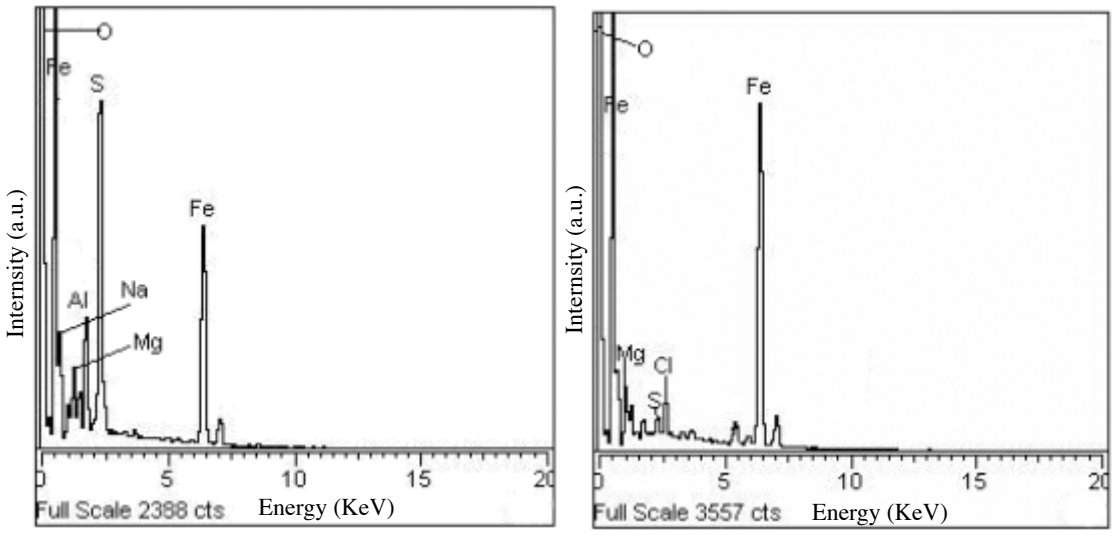
The combination of mix-culture (SSVSRB1 & 2) showed the highest shifted OCP values and leads high end point value of about –372 mV_{SCE} (after 15 days of exposure) compared else. This ennoblement shown in mix-culture could be due to the cathodic reaction as a result of a significant decrease of pH under biofilm and survival of the SRB (Dexter 1995). It has been reported that corrosion appears to be worsen when a wide variety of microorganisms are present (Franklin et al. 1989). The pure cultures usually induced higher corrosion rates initially, but with time the corrosion rates decreased compared to that of the control (Anderko & Shuler 1997).

SEM micrographs of steel surface after 15 days of exposure to the VMNI medium inoculated with SRB are presented in Figure 4. Microbiological data showed that higher number of SRB was associated with corroding sections of steel (Figure 4(a)) compared with non-corroding sections (Figure 4(b)). Electrochemical measurement conducted in the laboratory further proved



(a) (b)

FIGURE 4. SEM micrographs of stainless steel surface after three days of exposure to the VMNI medium inoculated with SRB (a) Corroded section (b) Non-corroded section (Magnification: 2500x) as refer to text for 'X' and 'Y'



(a) (b)

FIGURE 5. Energy dispersive X-ray analysis of (a) point X and (b) point Y shown on Figure 4

that in the presence of SRB, high corrosion rates of steel have been recorded (reported in previous paper). However, according to Franklin et al. (1989) the corrosion rates are not directly correlated with the total microbial biomass or the number of species.

Corroded and non-corroded sections of coupon immersed in VMNI medium inoculated with SRBs were analysed by EDAX. Two regions were examined and showed as point 'X' (Figure 4a) and 'Y' (Figure 4b), respectively. The biofilms and corrosion product forms together with the bacterial colonies around observed in Figure 4(a). EDAX data for both areas are given in Figure 5. The strong peaks of Fe, O and S observed on corroded section (Figure 5a), which indicates iron sulphur or iron oxide compounds were presence on this area. The appearance of S peak is due to the presence of iron sulphide formed as a result of SRB metabolic activities. It is well known that the higher concentration of iron sulphide in the corroded product indicates the influenced of SRB in the corrosion processes. The iron sulphide layer was formed on metal surface by Fe^{2+} reacting with hydrogen sulphide produced by SRB (Videla 1990).

CONCLUSION

In the presence of SRBs, the potential, E_{oc} shifted towards more positive values which are more noble compared to that in sterile. A high amount of elemental sulphur was detected as corrosion products in the presence of SRBs.

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