The Influence of Marine Sulphate-Reducing Bacteria, *Desulfovibrio sp.* on the Corrosion of AISI 304 Stainless Steel

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ABSTRACT

The influence of the sulphate-reducing bacteria isolated from MSE, Pasir Gudang, grown in VMNI medium, on the anaerobic corrosion of AISI 304 stainless steel was evaluated. Potentiodynamic polarizations and electrochemical impedance spectroscopy (EIS) were performed, both in the inoculated and in the sterile media. Scanning electron microscopy (SEM), energy dispersive analysis spectroscopy (EDS) and X-ray diffraction (XRD) were used to study the morphology and identify the corrosion product film. Tafel analysis of the polarization curves around the corrosion potential, E_{corr} showed that the presence of SRB induced changes in the corrosion potential in VMNI media. Results show that the EIS technique can be used to study mechanisms of corrosion and surface passivity. The experiments were complemented with surface analysis, which SEM observation of stainless steel coupons exposed to the SRB action, revealed bacteria present, as well as damaged steel surface. A type of localized corrosion was observed on the stainless steel surface, and it was associated to the SRB effect. An electrochemical measurement also showed that strong acceleration in pitting corrosion process occurred was induced by SRB. Analysis of EDS spectra indicates high counts of sulphur presence in coupon exposed in VMNI inoculated with SRB.

ABSTRAK

Kakisan anaerobik ke atas keluli tahan karat bersiri 304 di bawah pengaruh bakteria penurun sulfat yang dipencilkan dari MSE, Pasir Gudang yang dikulturkan dalam medium VMNI telah dikaji. Pengutuban keupayaan dinamik dan spektroskopi rintangan elektrokimia (EIS) telah dijalankan bagi kedua-dua sampel yang mengandungi medium bakteria berkultur dan medium steril. Mikroskop imbasan elektron, spektroskopi analisis tenaga penyebaran dan penyerakan sinar-X digunakan untuk kajian morfologi dan mengenal pasti filem produk kakisan. Analisis Tafel terhadap lengkuk pengutuban di sekitar keupayaan kakisan, E_{corr} *menunjukkan kehadiran SRB dalam medium VMNI cenderung berlakunya perubahan dalam keupayaan kakisan. Keputusan juga menunjukkan kaedah EIS boleh menerangkan mekanisma kakisan dan kepasifan suatu permukaan logam. Kajian ini juga turut dilengkapkan dengan analisis permukaan. Mikroskop imbasan elektron terhadap kupon keluli tahan karat yang terdedah kepada SRB mendapati terdapat kerosakan pada permukaan. Kakisan jenis setempat terbentuk pada permukaan yang boleh dikaitkan dengan SRB. Ujian elektrokimia membuktikan bahawa SRB merangsang mempercepatkan proses kakisan berlubang untuk berlaku. Analisis spektra EDS menunjukkan kepekatan sulfur yang tinggi pada kupon yang didedahkan dalam medium VMNI mengandungi SRB.*

Keywords: Sulphate-reducing bacteria; *Desulfovibrio sp.*; stainless steel; Tafel analysis; electrochemical impedance spectroscopy; scanning electron microscopy; energy dispersive analysis spectroscopy; localized corrosion and pitting.

Introduction

The susceptibility of the series 304 stainless steel to microbiological corrosion or MIC has been studied extensively in the literature (Stott 1993; Costerton et al. 1995; Dexter 1995; Gerchakov et al. 1986; Scotto et al. 1985; Dexter et al. 1991; Urquidi et al. 1986; Urquidi et al. 1991). Type 304 stainless steel has been used increasingly for offshore device, chemical, petrochemical and power utility industries. This has often been done to eliminate the need for corrosion inhibitors, with their environmental concerns. The excellent corrosion resistance of stainless steel is due to the formation of a stable passive layer. Nevertheless, stainless steel is susceptible to localized corrosion by chloride ions and reduced sulfur compounds (Stott 1993).

The presence of microorganism on the metal surface often leads to highly localized changes in the concentration of the electrolyte constituents, pH and oxygen levels (Costerton et al. 1995; Dexter 1995; Gerchakov et al. 1986). These microorganisms and their metabolic activity were clearly believed to influence the corrosion process (Scotto et al. 1985). Microorganisms often stimulate localized forms of corrosion, such as pitting, depending on the passive film forming and repairing capabilities of the metal or alloy (Dexter et al. 1991).

Sulfate-reducing bacteria (SRB) are usually part of the indigenous community of microorganisms in an ecosystem and are of great utilitarian and academic interest. They are of significant economic sectors and environmental concern because of their roles in anaerobic corrosion of steel and contamination of petroleum products. The role of SRB in anaerobic corrosion processes is indisputable (Stott 1993; Costerton et al. 1995; Dexter 1995; Gerchakov et al. 1986). Corrosion processes involve biotic and abiotic factors. The corrosion of stainless steel in marine systems, for example, is influenced by micro organisms and may be entirely biotic. The process of corrosion is directly linked to the growth and activities of these bacteria.

The presence study is designed to gain better understanding of the influence of SRB on the stability of stainless steel using electrochemical impedance spectroscopy (EIS), Tafel plots, scanning electron microscopy (SEM), energy dispersive analysis spectroscopy (EDS) and X-ray diffraction (XRD) techniques. SEM, EDS and XRD have been widely used in microbiologically influence corrosion study to obtain elemental information on corrosion products on metal surfaces (Lee & Characklis 1993; Jeffrey & Melchers 2002).

EIS and Tafel plots were used to investigate the electrochemical behaviour and to measure the polarization resistance of stainless steel. To identify the corrosion product film, SEM was used to study the morphology. EDS was used to determine the different elements in the film and their relative abundances. XRD was carried out to determine the chemical composition of the corrosion products and microbiological deposits. XRD also has been used to detect type of sulfide mineral (ferrous rust) compound among corrosion products of steel exposed to mediums containing SRB (Lee & Characklis 1993; Jeffrey & Melchers 2002; Olowe et al. 1991).

Materials and Methods

Cultural Conditions

The *Desulfovibrio sp.* used in this work was taken from Malaysian shipyard of Engineering, 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 Posgateô s Marine medium C (Zinkevich et al. 1996). The media 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 121^{o}C. It was left to cool to room temperature before being inoculated with the *Desulfovibrio sp.*

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

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
Yeast extract	2.0
Lactate	6.0
Ascorbic acids	0.1
Thioglycollic acid	0.1
$FeSO_4.7H_2O$	0.5
Trace elements (stock solution)	1.0 ml
Vitamins (stock solution)	2.0 ml

Electrochemical Experiments

These experiments were carried out in a ASTM standard cell (ASTM 1999), with three electrode systems: low carbon alloy steel as working electrode graphite rod as counter electrode and saturated calomel electrode as reference electrode (Fig. 1). The electrolyte used was 300 ml VMNI medium. Nitrogen gas was bubbled to remove all the oxygen and maintain anaerobic conditions. The carbon alloy steel samples (as a working electrode) were immersed in the electrolyte solution exposing a circular area of about 0.708 cm^2. All the experiments were performed using Autolab PGSTAT30. The electrochemical cell was connected to an Autolab PGSTAT30 and PC was used for data recording. All experiments were performed at 35^{o}C and during this time, several polarization resistance tests were carried out.

A potentiodynamic method was used to obtain the potential-current ratio, applying ± 10 mV over potential, with respect to the free corrosion potential, E_{corr}. The ǿGeneral purpose Electrochemical Systemô (GPES) software programs were used for data management and analysis.

(a) (b)

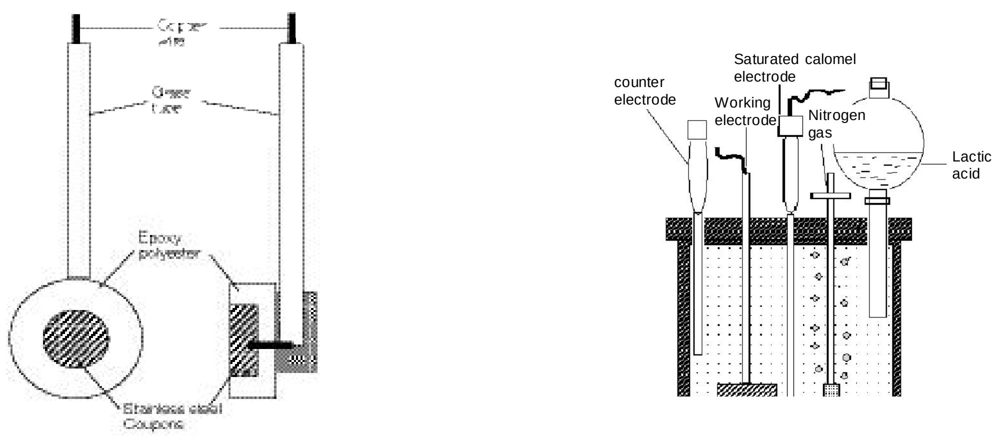


FIGURE 1: (a) Schematic Diagram of Stainless Steel Concentric Electrode (as a Working Electrode) and (b) Sketch of the Electrochemical Cell

From this technique, resistance values are obtained (R_p), which are used to calculate the corrosion current density, according to the following equation:

$$I_{corr} = \frac{B}{R_p}$$

Where B is the Tafel slope Faradaysô law which can be used to relate the corrosion current density to the corrosion rate, with the next equation:

$$\text{Corrosion rate (CR)} = \frac{K \times I_{corr} \times EW}{D}$$

Where K is constant = 3272, EW is equivalent weight and D is density.

The impedance measurements were carried out on computer-interfaced Autolab PGSTAT 30 equipment (Eco. Chemie B. V., Netherlands) together with frequency response analysis (FRA) system software for data management and analysis. The applied voltage amplitude was 5 mV at frequencies range between 1 and 100 kHz for EIS measurement. The conductivity was calculated by:

$$\sigma = \frac{1}{R_b} \times \frac{\lambda}{A}$$

where R_b is the bulk resistance from AC impedance, A the area of electrode and l the film thickness.

ESEM and EDS Studies

For SEM observation, the coupons were attached to a 3/8ò diameter aluminium stub using double sided tape and imaged using an ElectroScan model Leo 1455, (made in

Germany) and Philips XL30 (Made in United Kingdom) Variable Pressure SEM. The stage temperature was maintained at 8°C and the chamber pressure adjusted to keep the samples hydrated, typical values being in the range of 6.2 Torr. Dehydration was accomplished by reduction of the chamber pressure to 1.0 Torr and the process evaluated by monitoring the change in stage temperature due to evaporation from the sampleõs surface.

XRD Study

This technique is considered as the most reliable method for identification of corrosion product on the surface of coupons. The identification is based on the measurement of atomic structures obtained from their x-ray diffraction pattern of diffractogram. The identification of corrosion product was carried out using XRD model D8 Advance, Bruker and some parameter set-up as follows: theta wide scan = 10.0-90.0.; step size = 0.050; divergence = 0.5 degree and artiscatting = 0.5 degree. After immersion in natural environment or culture (simulated experiments) with varying periods, the AS and SS cylindrical coupons (9.5 mm diameter × 6.0 mm) were nitrogen-dried without rinsing gently to avoid surfaces disturbed and hydrated with incubated in 30°C for over night before XRD tested.

Results and Discussion

Potentiodynamic anodic and cathodic polarisation curves of alloy steel around E (I = 0) in the active potential region has been recorded at 10 mVs^{-1} to allow steady-state current. This curve are given in a semi-logarithmic form (Figure 2) from the extrapolation of the Tafel lines corrosion potentials (E_{corr}) and corrosion current densities (I_{corr}) for the VMNI medium sterile and VMNI containing SRB. The corresponding values are given in Table 2. The data clearly shows that, the addition of SRB influence the E_{corr} and I_{corr} with the parameters change drastically after 8 days of exposure.

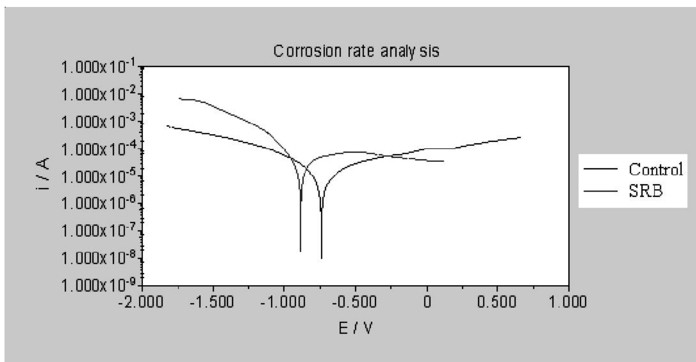


FIGURE 2: Tafel Plots of the Quasi-steady Polarisation Curves of Stainless Steel in the VMNI Medium (control) and Containing of SRB at 37°C for 8 Days Exposure

TABLE 2: Corrosion Tafel Data for Stainless Steel in VMNI Medium (Control) and Containing of SRB at 37⁰C for 8 Days Exposure

Solution	E_{corr} (V vs. *sce*)	I_{corr} (µAcm^{-2})	Corr. rate (mmpy)	β_a (V/dec)	β_c (V/dec)
Control	-0.74	3.56E-5	4.94E-2	1.43	0.55
SRB	-0.89	4.64E-5	6.75E-2	0.54	0.21

From Figure 2, the position of Tafel plot curves for SRB is more anodic direction compared to control. It was also observed that the corrosion potential value of VMNI medium with *Desulfovibrio sp.* inoculated was more ennoblement (more less anodic values) (E_{corr} = -0.89 V(SCE)) compared to control (E_{corr} = -0.74 V(SCE)). Meanwhile, the current density is higher (I_{corr} = 4.64E-5 µAcm^{-2}) for VMNI inoculated with *Desulfovibrio sp.* compared to control (I_{corr} = 3.56E-5 µAcm^{-2}).

The anodic and cathodic Tafel slope values for VMNI medium with SRB inoculated are as low as 0.54 and 0.21 V/dec, respectively. While for control, the anodic Tafel slope of approximately 1.43 V/dec was obtained and cathodic Tafel slope of approximately 0.55 V/dec was also obtained. The corrosion rates of VMNI medium containing *Desulfovibrio sp.* was only slightly high (0.068 mmpy) compared to control (0.049 mmpy).

Figure 3 shows the Nyquist plots of EIS spectra for stainless steel immersed in sterile VMNI (control) and VMNI containing SRB1 for 8 days exposure. It is obviously that the higher of semicircle size observed in control compared to the presence of SRB. The polarization resistance of semicircle were about of 92400 and 7170 ohms for large and small respectively.

Comparative Bode graphs for corrosion stainless steel with and without SRB1 during the study on the 8 days of immersion is presented in Figure 4, which showed different phase angle and slightly time constant response throughout the test period in sterile and with the presence of SRB1. The phase angles in Figure 4 are (φ_1 = 161.1°, φ_2 = 135.2°) and (φ_1 = 89.8°, φ_2 = 100.0°) for the large and small semicircles, respectively. The lowest

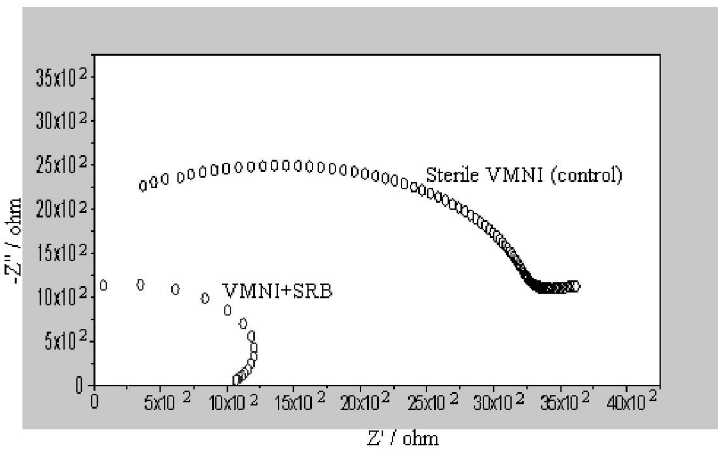
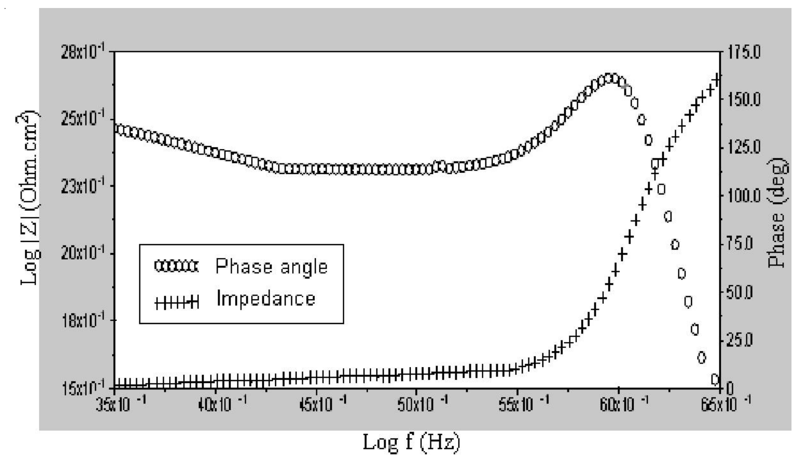


FIGURE 3: Nyquist Plots for Corrosion of Stainless Steel with VMNI Inoculated with SRB and Sterile VMNI (control) During the Study on the 8 Day of Immersion

TABLE 3: EIS Data for Corrosion of Stainless Steel with VMNI Inoculated with SRB and Sterile VMNI (Control) During the Study on the 8 Day of Immersion

Solution	R_p (ohms)	φ_{max} (°)	T = log f (Hz)
Sterile VMNI	9.24E+04	φ_1 = 161.1 φ_2 = 135.2	t_1 = 6.1 t_2 = 3.5
VMNI+SRB	7.17E+03	φ_1 = 89.8 φ_2 = 100.0	t_1 = 5.9 t_2 = 4.0

(a)



(b)

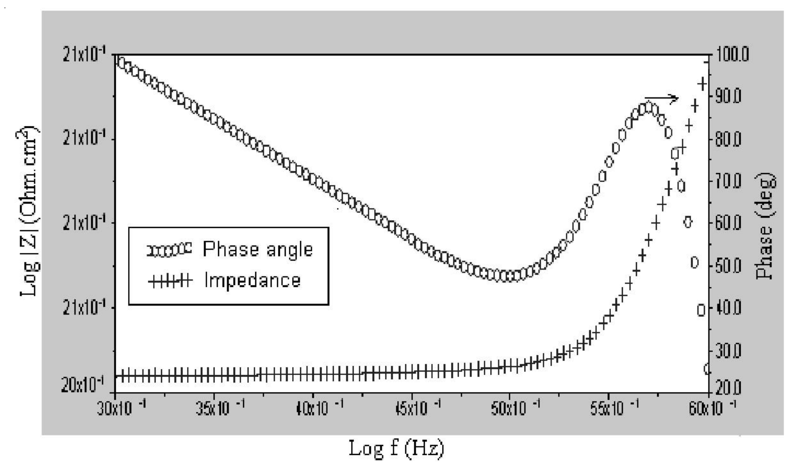
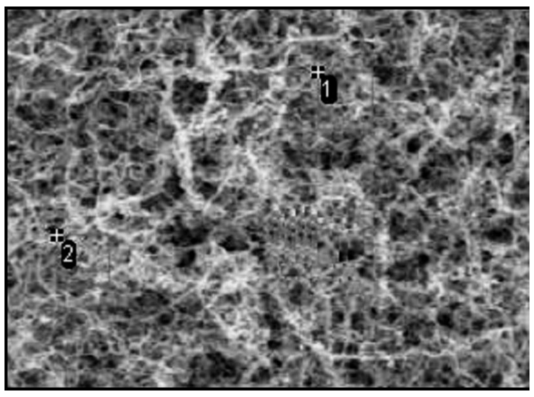


FIGURE 4: Comparative Impedance Spectra for Corrosion Stainless Steel During the Study on the 8 Day of Immersion: (a) Bode Graphs for the Sterile VMNI (Control) and (b) Bode Graphs for VMNI Inoculated with SRB

phase angle was to be found in the presence of SRB which indicate the less protective passive layer. The presence of SRB influenced the solution/steel interface and the non-compact passive layer formed to allow of diffusion of ions through between the surface and solution.

SEM images and EDS were prepared from a number of surface coupons recovered from the sterile and inoculated with SRB in VMNI medium after periods of experiments. Figure 5 shows the SEM and EDS deposits on the surface of stainless steel in sterile VMNI (control) after 15 day exposure and concentration of metal species are listed in Table 4. The EDS analysis reveals that on the deposits were composed by mixed compounds of Cl, Na, Fe, O, Mg and S. The strong iron peaks appear in Figure 5 because EDS electron could penetrate the thin surface layer to reach the Fe metal underneath. Oxygen peaks as a second higher observed (Table 4) due to the presence of oxide in deposits of corrosion product layers. The strong presence of Na, Mg and Cl indicates that those salts were the main precipitate in VMNI medium.

(a)



(b)

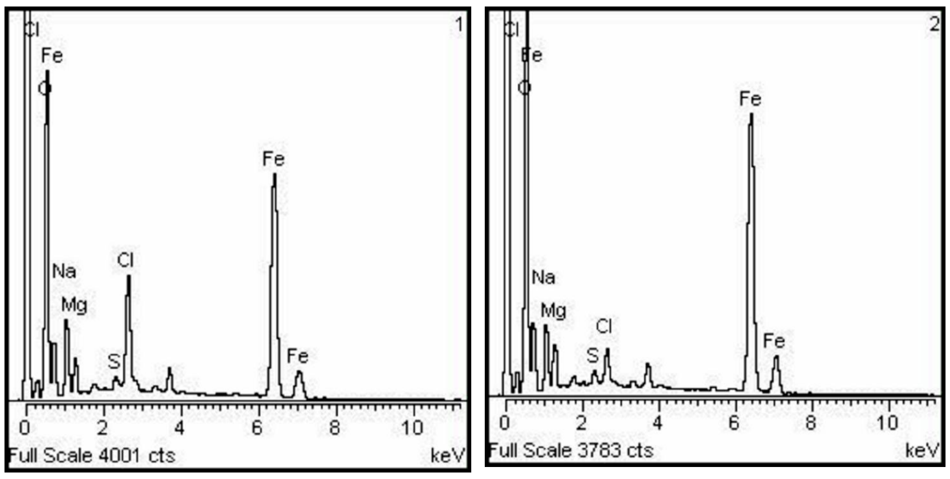


FIGURE 5: (a) SEM Images of Deposits on the Surface of Stainless Steel in Sterile VMNI (control) After 15 Day Exposure and (b) EDS Spectra of These Deposits

TABLE 4: Concentration of Metal Species (count per seconds, CPS)

Spectrum	O	Na	Mg	S	Cl	Fe	Total
1	34.71	9.04	3.06	0.66	7.32	45.21	100.00
2	33.98	7.70	3.72	0.68	2.05	51.87	100.00
Max.	34.71	9.04	3.72	0.68	7.32	51.87	
Min.	33.98	7.70	3.06	0.66	2.05	45.21	

The SEM and EDS deposits on the surface of stainless steel in VMNI inoculated with SRB after 15 day exposure presented in Figure 6 and concentration of metal species are listed in Table 5. The strong peaks of Fe, O and S, as seen in Figure 6, indicate the presence of iron sulphur or iron oxide compounds. The appearance of S peak is due to the presence of metal sulphides formed as a result of SRB metabolic activities.

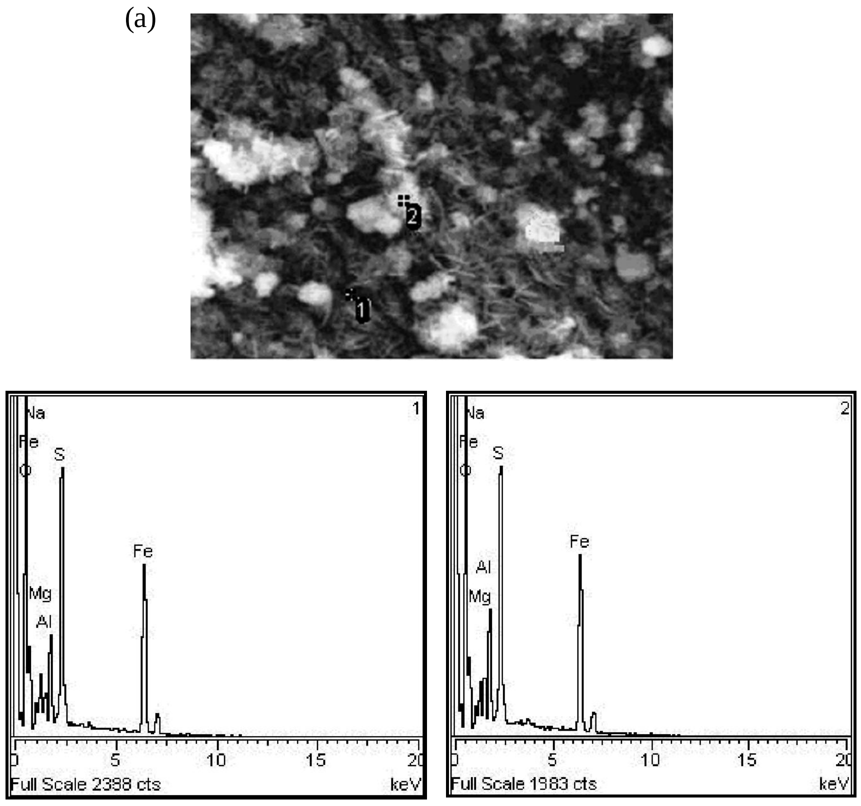


FIGURE 6: (a) SEM Images of Deposits on the Surface of Stainless Steel in VMNI in the Presence of SRB After 15 Day Exposure and (b) EDS Spectra of Black Film of Corrosion Products

TABLE 5: Concentration of Metal Species (count per seconds, CPS)

Spectrum	O	Na	Mg	S	Cl	Fe	Total
1	23.73	1.76	7.48	17.63	1.65	47.75	100.00
2	24.67	1.89	6.33	15.21	2.63	49.27	100.00
Max.	24.67	1.89	7.48	17.63	2.63	49.27	
Min.	23.73	1.76	6.33	15.21	1.65	47.75	

It is well-known that high concentration of sulphide in corrosion product indicate that the influenced of SRB in corrosion processes. The ferrous sulphide layer is formed on metal surface by Fe^{2+} reacting with hydrogen sulphide produced by SRB (Videla 1990). Figure 6(a) shows more detail of the black iron sulphide region. It was taken from the area that was closest to the metal surface and which appeared as a black deposit. As confirmed by the EDS in Figure 6(b), the deposits were form of iron sulphide.

X-ray difraction (XRD) was carried out to identify the elemental information on corrosion products on metal surfaces. XRD analysis of coupons with this corrosion product confirmed as iron oxide (Fe_2O_3) for sterile and mackinawite (tetragonal FeS_{1-x}) for inoculated of SRB. The presence of mackinawite or greigite among corrosion products of iron is an evidence that SRB participated in the corrosion reaction (Jack et al. 1985; McNeil et al. 1991; Beech & Gaylarde 1999). The initial corrosion product formed as far as SRB is concerned is mackinawite, an iron rich sulphide, that forms a poorly protective layer on the metal surface. This is in aggrement with results of Rodriguez et al. (2002).They found that the sulphide formed on steel was most unprotected in the pH range 6.5-8.8, which mackinawite being the only corrosion product.

According to Jeffrey and Melcher (2002), mackinawite is a particular form of iron sulphide that appears to occur frequently in immersion corrosion studies. It also suggests that mackinawite are most likely to be observed in seawater-related corrosion. It is known that mackinawite is produced easily from iron and iron oxide by consortia of microorganisms including SRB (Hamilton 1994). Moreover, the presence of mackinawite in corrosion products formed in SRB culture is indicative of SRB-induced corrosion. Recent work indicates that on continued exposure to SRB, mackinawite alters to greigite (Fe_3S_4), smythite (Fe_9S_{11}) or to pyrrhotite ($Fe_{1-x}S$) where [0 = x = 0.2].

During all electrochemical experiments with the presence of SRB, a black film of corrosion product formed on the coupons steel surface. In the sterile cell system, a slightly brown colour appeared on the surface corrosion product. Beech et al. (1999) and Jeffrey & Melcher (2002) used ESEM, EDX and XRD to identify the black corrosion film as mackinawite, greigite, smythite and pyrrhotite, in their study. In the present study of marine SRB culture, SEM and EDS studies confirmed that the film was made up of sulfides, and XRD analysis indicated that mackinawite was the main component on surface corrosion products.

After the removal of the corrosion products layer (performed to ASTM corrosion testing standards), samples of both steels were studied using SEM. Images of surface morphology were observed in the absence and presence of sulphate reducing bacteria. In Figure 7(a), SEM photo shows no significant localized corrosion are to be observed after 15 days exposure. This result indicates that the VMNI medium has no ability to corrosion pitting occur for stainless steel. The excellent corrosion resistance of stainless steel was due to the formation of a stable passive layer.

SEM micrographs of surface morphology for stainless steel after 15 days exposed in VMNI with presence SRB are presented in Figure 7(b). The pitting showed up on the inner layer of stainless steel as sites of localized corrosion. It is well known that deposits can enhance localized corrosion of stainless steel. Nevertheless, stainless steel is susceptible to localized corrosion by chloride ion and reduced sulfur compounds (Stott

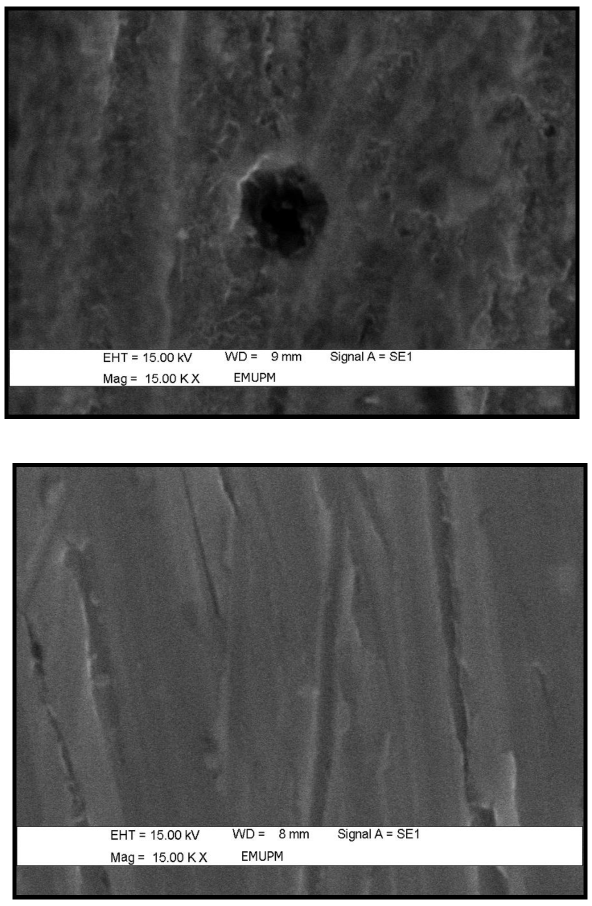


FIGURE 7: SEM Micrograph of Typical Pits after Removing the Corrosion Products for Stainless Steel at (a) VMNI (sterile) (b) VMNI Inoculated with SRB; After 15 Days of Immersion, 15,000x.

1993). The presence of SRB on metal surface often leads to highly localized changes in the concentration of the electrolyte and pH level (Costerton et al. 1995; Dexter 1995; Gerchakov et al. 1986). SRB often stimulate localized forms of corrosion, such as pitting, depending on the passive film forming and repairing capabilities of the steel (Dexter et al. 1991).

Conclusions

SRB1 isolated from MSE, Pasir Gudang have been shown to influence the corrosion of 304 series stainless steel. Stainless steel is relatively unstable in the presence of sulphate-reducing bacteria colony. The large corrosion micropits (± 30 µm diameter) were observed for stainless steel in the presence of the *Desulfovibrio sp.*. The presence of SRB has led to a significant decrease in the value of R_p, gives rise to corrosion rate and localized corrosion.

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