



Corrosion Behavior of Mild Steel in Seawater from Northern Coast of Java and Southern Coast of Bali, Indonesia

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Abstract. The corrosion behavior of mild steel in seawater was investigated using an immersion test and energy-dispersive X-ray spectroscopy in solutions from the sites of Muara Baru, Suramadu and Tol Mandara. As reference, solutions of 3.5% and 5% NaCl were prepared. Dissolved oxygen, salinity, conductivity, and total dissolved solids (TDS) were measured. It was found that uniform corrosion occurred on the mild steel during the immersion test. The corrosion resistance of the steel decreased with increasing exposure time. Since the magnitudes of conductivity, salinity and TDS of all test solutions were similar, it was concluded that dissolved oxygen (DO) and chloride ions play an essential role in inducing the corrosion risk of mild steel. Both parameters hinder the formation of a stable passive film on the surface of corroded mild steel.

Keywords: *conductivity; dissolved oxygen; immersion test; mild steel; salinity; seawater; total dissolved solids.*

1 Introduction

Mild steels are the most commonly applied structural materials in various industries due to their mechanical strength, easy manufacture, weldability, formability and reasonable cost. However, in more severe or aggressive environments, such as marine or seawater, mild steel is not sufficient. Instead, austenitic stainless steels such as 304 and 316 are chosen for application in such environments [1]. Furthermore, seawater is a complex chemical system that is affected by various factors, including concentration and access of dissolved oxygen, salinity, concentration of minor ions, biological activity and pollutants [2]. The corrosion of mild steel immersed in seawater is influenced by these factors [3]. Consequently, seawater specimens have different corrosivity depending on the sampling location of the bulk seawater mass [4]. The balance of organisms and dissolved organic nutrients starts to change as soon as a natural seawater specimen is isolated from the parent water mass. Therefore, natural seawater is not easy to simulate in the laboratory for corrosion-testing purposes. Hence, a solution of 3.5% NaCl is commonly applied for simulating

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seawater. This NaCl solution is known to be more aggressive than natural seawater, especially toward carbon steel [4].

Several researchers have already investigated the corrosion behavior of mild steel considering the parameters of dissolved oxygen, salinity, and temperature in sub-tropical regions [5-7]. In a southeastern region representative of tropical areas, Wan Nik and co-workers [8] have investigated the corrosion behavior of mild steel in seawater from the Kuala Terengganu coastal area. They found that differences in temperature and salinity cause different corrosion behavior of mild steel in coastal areas [8]. However, with regard to mild steel, there is little study on its corrosion behavior in tropical seawater. Therefore, the objective of the present work was to elucidate the corrosion behavior of mild steel in tropical seawater in various regions in Indonesia, more specifically the northern coast of Java and the southern coast of Bali, Indonesia.

2 Experiments

2.1 Sample Preparation

Specimens of mild steel were prepared (length 20 mm, width 20 mm, and thickness 1 mm). Prior to the experiments, the removal of corrosion products on the metal specimens was carried out by the pickling method according to ASTM G1-81. After that, the pickled specimens were cleaned and washed using distilled water and subsequently acetone, and then stored in vacuum desiccators. They were weighed for initial weight. Seawater as corrosive media was taken from different areas, i.e. the Muara Baru region (A) and the Suramadu coastal area (C), both on the northern coast of Java island, and the Benoa coastal area (B), as shown in Figure 1.



Figure 1 Various sites of seawater (A, B and C).

In addition, 3.5% NaCl and 5% NaCl solutions were prepared as reference solutions. The composition of the mild steel used is shown in Table 1.

Table 1 Chemical composition (wt%) of mild steel used.

Elements	Percentage
Carbon	0.051
Manganese	0.734
Silicon	0.126
Sulphur	0.004
Phosphorus	0.016
Iron	remainder

2.2 Weight Loss Analysis

Before the specimens were cleaned with the pickling solution, which contained hydrochloric acid and hexamethylenetetramine [9], they were weighed for initial weight by using an analytical balance (accuracy of 0.0001 g). After that, the specimens were immersed in seawater obtained from sites A, B and C. Each specimen was sampled out at a certain interval during the 1-month experiment. Before weighing, the specimens were cleaned with distilled water and immersed in pickling solution to remove the corrosion product. The specimens were washed with distilled water, dried and weighed in order to get the final weight.

Generally, carbon steels such as AISI 1040 when applied in immersed offshore structures are attacked by uniform corrosion [10]. Therefore, the calculation of the corrosion rate was done assuming uniform corrosion over all surfaces of the specimens. One method for the calculation of the corrosion rate is based on weight loss, as expressed in Eq. (1) as follows [11]:

$$CR \text{ (mm /y)} = 87.6 \times (W / DAT) \quad (1)$$

where W = weight loss in milligrams, D = metal density in g/cm³, A = area of sample in cm², T = time of exposure of the metal sample in hours.

2.3 Measurement of Seawater Parameters and Observation of Corroded Specimens

The major parameters of seawater that influence the corrosion rate of steel are: salinity, dissolved oxygen, pH, and temperature [12]. These parameters were considered in this work. The seawater parameters were measured using an HQ40d Advanced Portable Meter. This instrument is a handheld system for field measurement of dissolved oxygen (DO), salinity, conductivity, temperature, total dissolved solids (TDS), and pH. During the metal immersion experiment, the parameters were measured at a certain interval and compared between sites A, B and C. In addition, the observation of constituent distribution

on the surface of the corroded specimens was conducted by using energy-dispersive X-ray spectroscopy.

3 Result and Discussion

3.1 Relation of Weight Loss Analysis and Seawater Parameters

Figure 2 shows the changes in corrosion rate of the carbon steel obtained from immersion in seawater from the Muara Baru, Suramadu and Tol Mandara sites, respectively. The corrosion rates of carbon steel in 3.5 wt% and 5 wt% NaCl solutions are presented for comparison. The figure shows the immersion time dependence of the corrosion rate for the carbon steel in the different environments. The first phase is the initiation phase, which shows a drastic increase in corrosion rate at 7 days of exposure. The higher corrosion rate takes place due to the role of oxygen and chloride in electrochemical reactions [10]. Following the first phase, the corrosion rate decreased until about 20 days of exposure. The decrease in corrosion rate can be related to the formation of a passive film on the surface of the mild steel, which behaves as a protective layer against further corrosion. The corrosion rate increased slightly up to 20 days of exposure. A higher corrosion rate of carbon steel was observed in the 5 wt% NaCl solution compared with the seawater solutions as well as in the 3.5 wt% NaCl solution, even though the corrosion rate decreased at 15 and 21 days of exposure, respectively. Overall, it was found that the corrosion resistance of carbon steel tends to increase with the increase of immersion time up to 1 month of exposure.

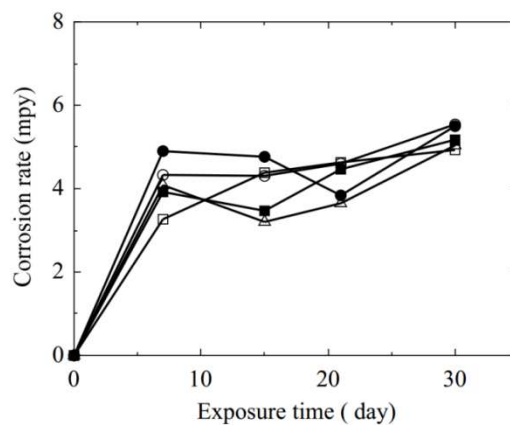
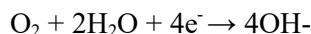


Figure 2 Corrosion rate of mild steel as function of exposure time in the solutions containing \circ 3.5% NaCl; \bullet 5% NaCl; \square seawater from Muara Baru; \blacksquare seawater from Suramadu; and \triangle seawater from Tol Mandara.

The magnitude of dissolved oxygen (DO) of different solutions before exposure was higher than after exposure, as shown in Figure 3. At 7 days of exposure, the DO of all solutions decreased with increasing corrosion rate, because of the cathodic reduction of dissolved oxygen taking place in neutral solution conditions in the following reaction:



From 7 days to 30 days of exposure, DO increased slightly, while the corrosion rate in all solutions also increased in this period.

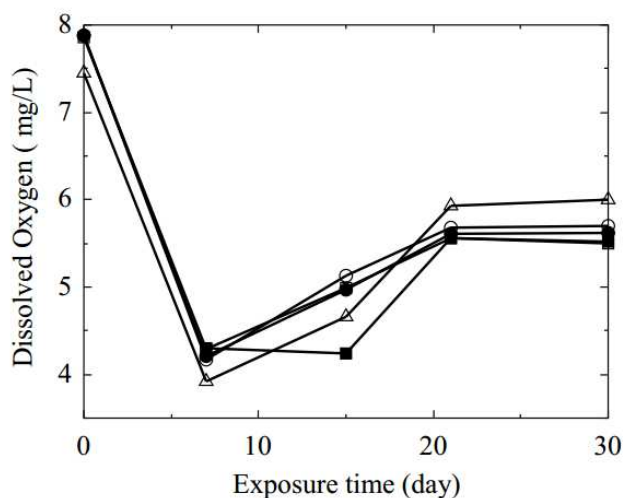


Figure 3 Dissolved oxygen level as function of exposure time in the solutions containing ○ 3.5% NaCl; ● 5% NaCl; □ seawater from Muara Baru; ■ seawater from Suramadu; and △ seawater from Tol Mandara.

Furthermore, higher corrosion rates of carbon steel at different sites occurred after 7 days of exposure, when the content of DO had decreased. In addition, the maximum solubility of DO in water is relatively low, about 8 ppm at ambient temperature, where the corrosion is controlled by diffusion of dissolved oxygen on to the steel surface [4]. The oxidation reaction of ferrous ions proceeds rapidly as oxygen reaches the metal surface [13]. This implies that the oxygen level decreases due to the consumption of oxygen and the limited oxygen level at stagnant solution. After 7 days of exposure, the dissolved oxygen content increased slightly up to 1 month of exposure. The magnitude of the corrosion rate for the different solutions also slightly increased up to 1 month of exposure, where chloride ions contributed to the breakdown of passive film (e.g. ferrous oxide) on the surface of the steel. The breakage of the passive film is an active site for anodic reactions.

Figure 4 shows salinity as a function of exposure time in different solutions at ambient temperature. The salinity of the 5% NaCl solution and seawater from Muara Baru, Suramadu and Tol Mandara was similar, while for the 3.5% NaCl solution it was lower. Salinity is evaluated by determination of the $[\text{Cl}^-]$ ion concentration in the water, which empirically states that salinity equals $1.80655 \times [\text{Cl}^-]$ [14]. It should be noted that Cl^- ions in seawater are correlated mainly to the NaCl, MgCl_2 and KCl content [15]. Therefore, the seawater from the Muara Baru, Suramadu and Tol Mandara sites had higher salinity compared to the 3.5% NaCl solution. Higher salinity means lower oxygen solubility. It is known that an increase of dissolved oxygen can increase corrosion risk. However, on the basis of the present results, the magnitude of salinity in the different seawater samples was almost the same at various exposure times. Therefore, the corrosion risk of the steel in all the test solutions did not depend on the salinity.

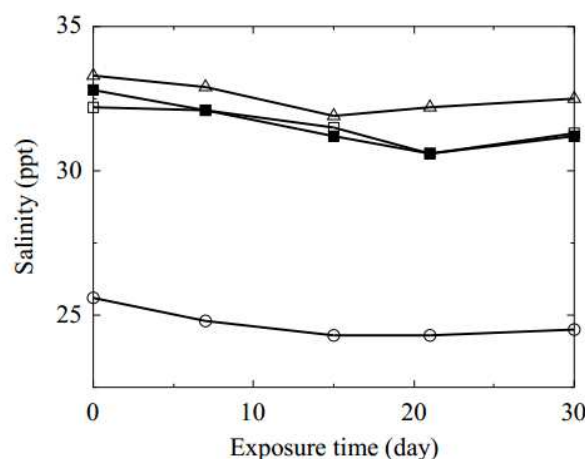


Figure 4 Salinity level as function of exposure time in the solutions containing \circ 3.5% NaCl; \bullet 5% NaCl; \square seawater from Muara Baru; \blacksquare seawater from Suramadu; and Δ seawater from Tol Mandara.

Conductivity measurements were conducted. The conductivity was then converted into salinity using empirical relationships. Figure 5 shows electrical conductivity as a function of exposure time in the various solutions at ambient temperature. According to the results, the conductivity of the seawater from the different sites had almost the same level compared to both NaCl reference solutions. The 5% NaCl solution, which had the highest conductivity, showed a high total quantity of dissolved salt ions, in contrast with the 3.5% NaCl solution, which had the lowest conductivity. In addition, the conductivity of all test solutions had almost of the same magnitude for all exposure periods. The similar magnitude of conductivity in the different seawater sites points to a

similar concentration of dissolved ions or total dissolved various salts. Corrosion rates tend to increase when water conductivity increases [14]. However, the present results show that the corrosion rate of the steel in all test solutions tended to increase up to 1 month of exposure but there was no change in conductivity level in the solutions. It was concluded that the corrosion risk of steel does not depend on conductivity.

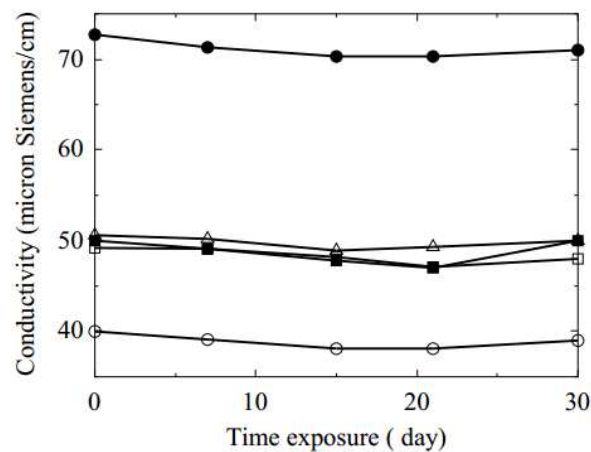


Figure 5 Conductivity as a function of exposure time in the solutions containing ○ 3.5% NaCl; ● 5% NaCl; □ seawater from Muara Baru; ■ seawater from Suramadu; and △ seawater from Tol Mandara.

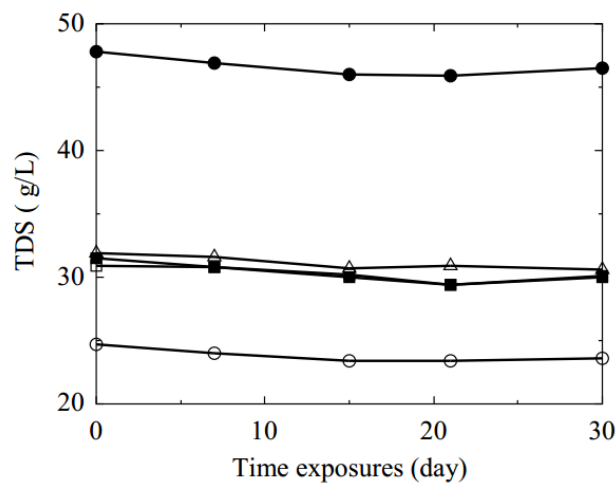


Figure 6 Total dissolved solids (TDS) as a function of exposure time in the solutions containing ○ 3.5% NaCl; ● 5% NaCl; □ seawater from Muara Baru; ■ seawater from Suramadu; and △ seawater from Tol Mandara.

Figure 6 shows total dissolved solids (TDS) as a function of exposure time in the test solutions. The TDS parameter quantifies both organic and inorganic compounds in the ionic, particle or colloidal states [16]. Water can be regarded as fresh ($\text{TDS} < 1,500 \text{ ppm}$), brackish ($1,500 \text{ ppm} < \text{TDS} < 5,000 \text{ ppm}$) or saline ($\text{TDS} > 5,000 \text{ ppm}$) [14]. All test solutions were categorized as saline solutions due to salinity higher than 5 g/L . The TDS measurement can be related to the conductivity as expressed in Eq. (2) as follows:

$$\text{TDS (ppm)} = \text{conductivity (uS/cm)} \times \text{conversion factor} \quad (2)$$

The HQ40d Advanced Portable Meter uses a conversion factor of around 0.64. The value of TDS is directly proportional to that of conductivity. Concerning the corrosion rate of steel, high levels of TDS enhance the corrosion risk. Furthermore, according to the results, the TDS in the different seawater sites was almost of the same magnitude compared to the reference salt solutions. The highest TDS for the 5% NaCl solution implies a high total quantity of dissolved salt ions, which did not occur in the solution with the lowest TDS, i.e. that of 3.5% NaCl. In addition, the TDS of all test solutions had almost the same level for all periods of exposure. Whereas the corrosion rate for steel in all test solutions tended to increase up to 1 month of exposure, no change of TDS levels occurred. This means that the corrosion risk of steel in all test solutions also did not depend on the TDS.

3.2 Element Distribution of Corroded Surface after Exposure

Figures 7 and 8 show the surface distribution of the elements in the steel samples after being exposed to the 3.5% and 5% NaCl solutions, respectively. The main element, Fe, was present uniformly. The presence of oxygen indicates that the surfaces were covered by a ferrous oxide film. On the other hand, the presence of the element of Cl on the surface indicates the presence of a salt film. In the presence of chloride ions, the outer layers of passive oxide films are displaced due to catalytic Fe^{3+} formation, where a two-step reaction takes place in which an intermediate metastable FeOCl film is displaced by a chloride island on the passive surface [17]. This means that the salt island (FeOCl) loosely adheres to the steel surface and thus cannot protect it from further corrosion attacks. This island acts as a potential active site (anodic site), where film breakdown occurs and the steel dissolves [17].

In the previous section, the corrosion rate of the steel in the various test solutions tended to increase up to 30 days of exposure. A corrosion product film on the surface of steel slows down the increase of the corrosion rate. For comparison, chloride ions destructive of the passive film [18] spread over the surface denser in the 5% NaCl solution than in the 3.5% NaCl solution.

Figure 9 shows the distribution of elements on the surface of the corroded steel after 1 month of exposure to the Muara Baru sample. The major element, Fe, was spread over the surface uniformly. The presence of elements such as Na, Mg and Cl is indicated by constituents of seawater such as NaCl and MgCl₂ [19]. Oxygen spread over the surface of the steel indicates the presence of corrosion products of oxide film. Cl was observed all over the surface. This implies that there are corrosion products containing metastable salt oxide on the surface.

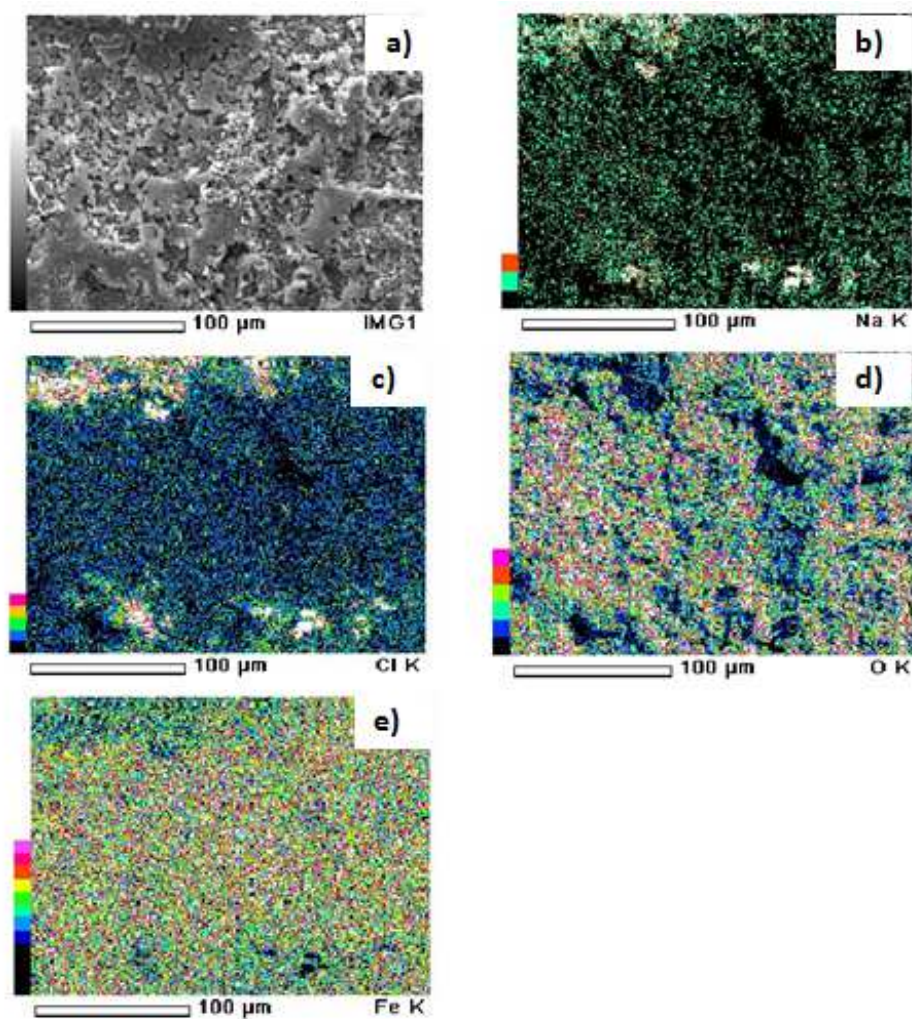


Figure 7 Distribution of elements on corroded steel surface after 1 month of exposure to 3.5% NaCl solution at ambient temperature.(a) SEM Image, (b) Na, (c) Cl, (d) O and (e) Fe.

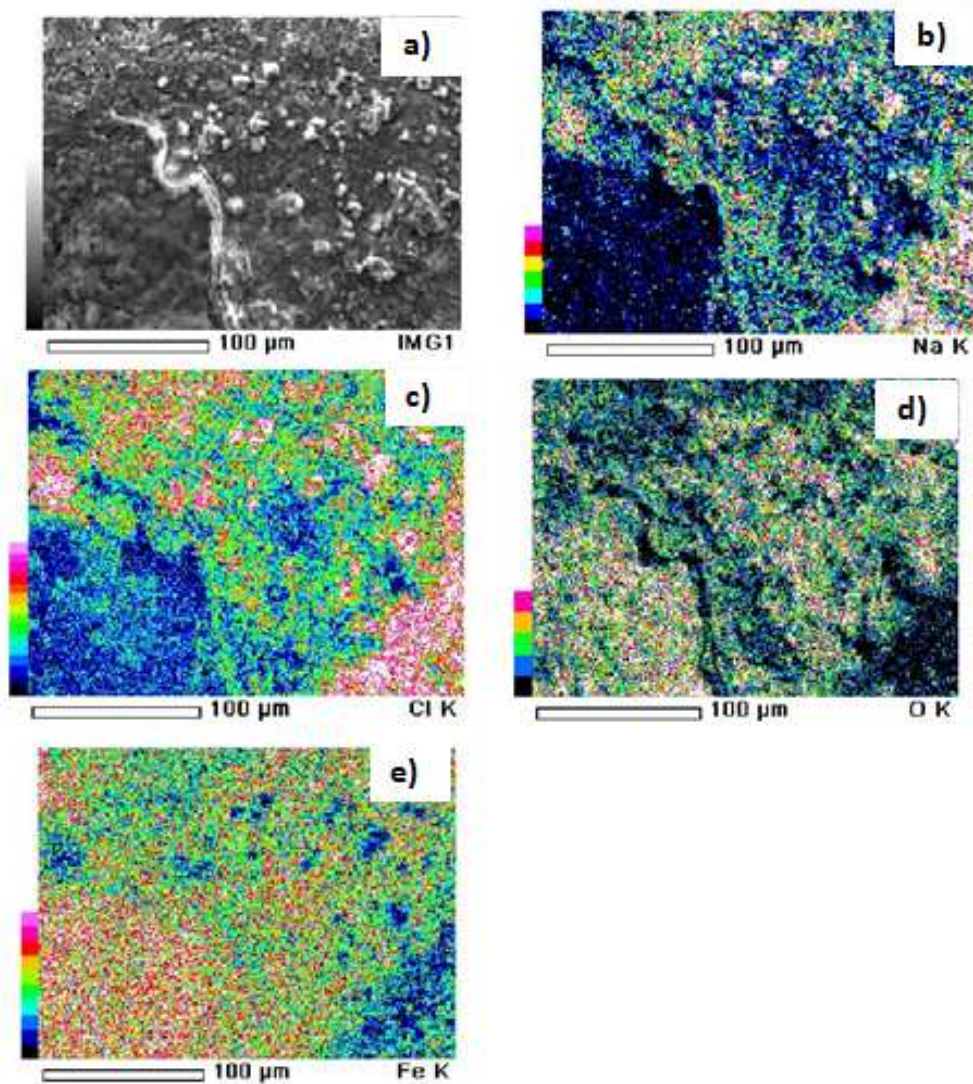


Figure 8 Distribution of elements on corroded steel surface after 1 month of exposure to 5% NaCl solution at ambient temperature. (a) SEM Image, (b) Na, (c) Cl, (d) O and (e) Fe.

Figure 10 shows the surface distribution of the elements of the carbon steel after exposure to the Suramadu solution. The major constituent, Fe, was spread over the surface uniformly, while the components of salt compounds were Na, Mg, and Cl from seawater. The presence of Ca kations was indicated by CaCl_2 compound in seawater [20]. In addition, oxygen covered the surface, which denotes corrosion products of oxide film. Furthermore, the tendency of a higher

corrosion rate of steel up to 1 month of exposure denotes the essential role of Cl ions as destructive ions causing oxide film breakdown.

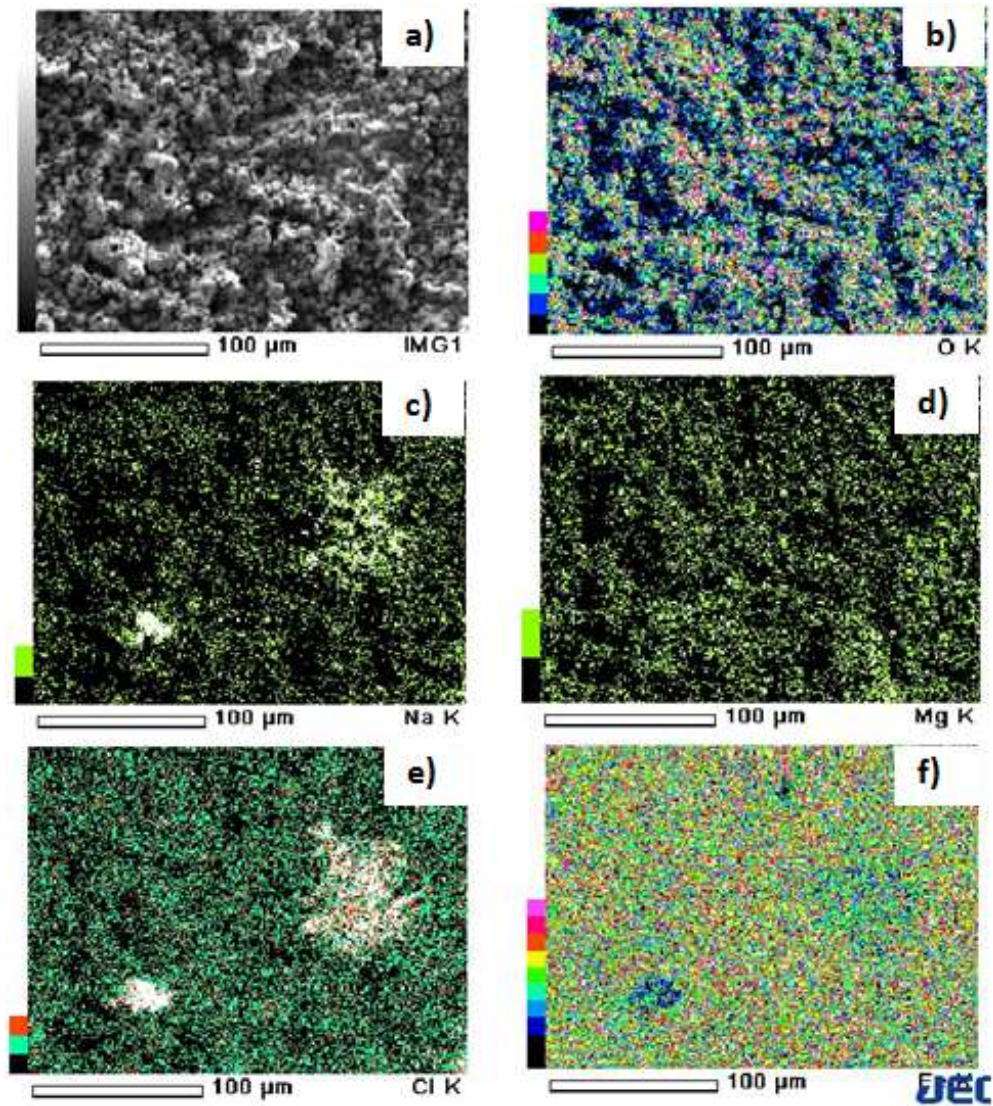


Figure 9 Distribution of elements on corroded steel surface after 1 month of exposure to Muara Baru solution at ambient temperature. (a) SEM Image, (b) O, (c) Na, (d) Mg, (e) Cl and (f) Fe.

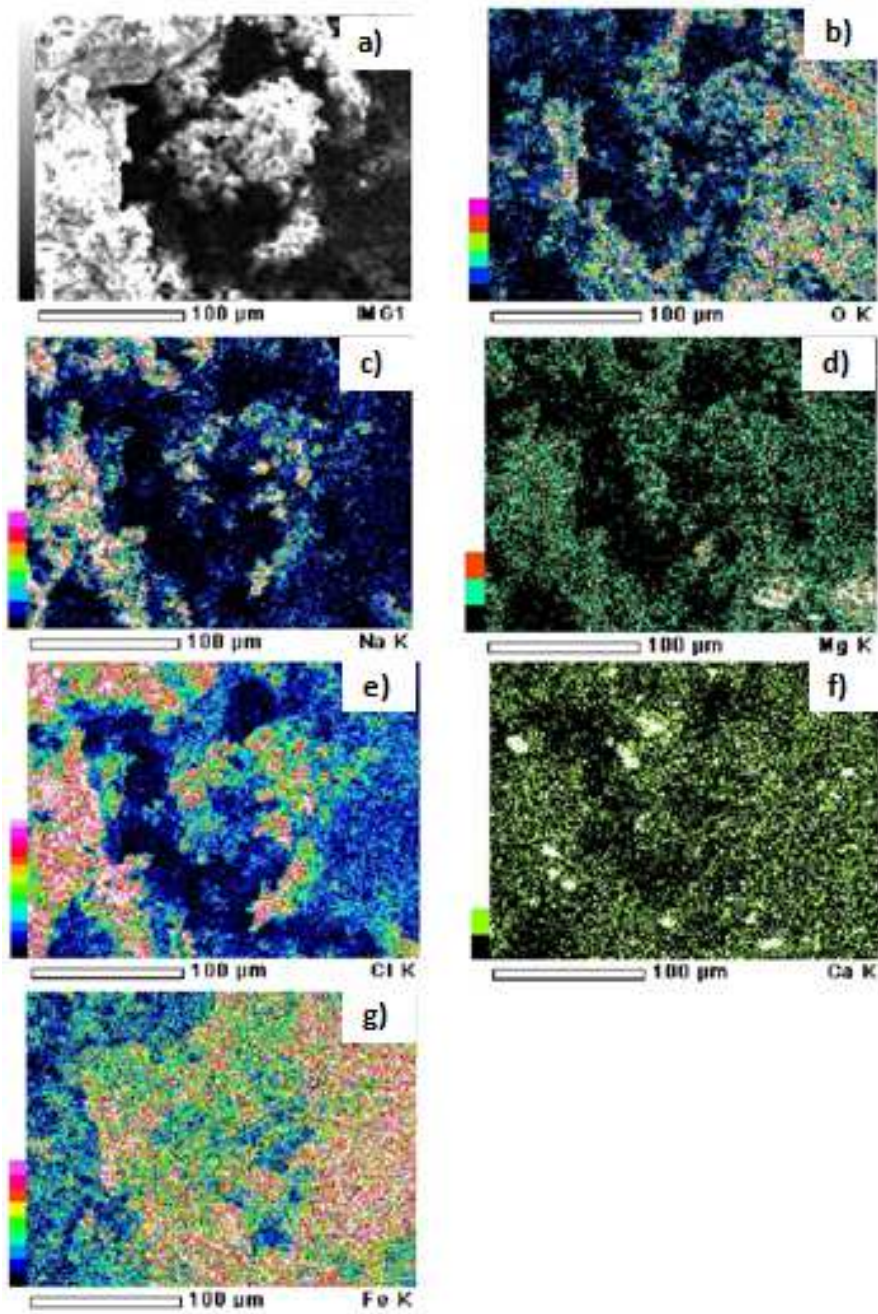


Figure 10 Distribution of elements on corroded steel surface after 1 month of exposure to Suramadu solution at ambient temperature. (a) SEM Image, (b) O, (c) Na, (d) Mg, (e) Cl, (f) Ca and (g) Fe.

Figure 11 shows the surface distribution of the elements of the carbon steel after exposure to the Tol Mandara solution. The main element, Fe, covered the surface uniformly, while the components of salt compounds were Na, Mg, and Cl from seawater. Oxygen was distributed all over the surface, which indicates corrosion products of oxide film on the surface. On the other hand, Cl ions contribute to the increase of the corrosion rate of steel. Furthermore, all morphologies of the corroded surfaces of mild steel were predominantly uniform in all test solutions after exposure.

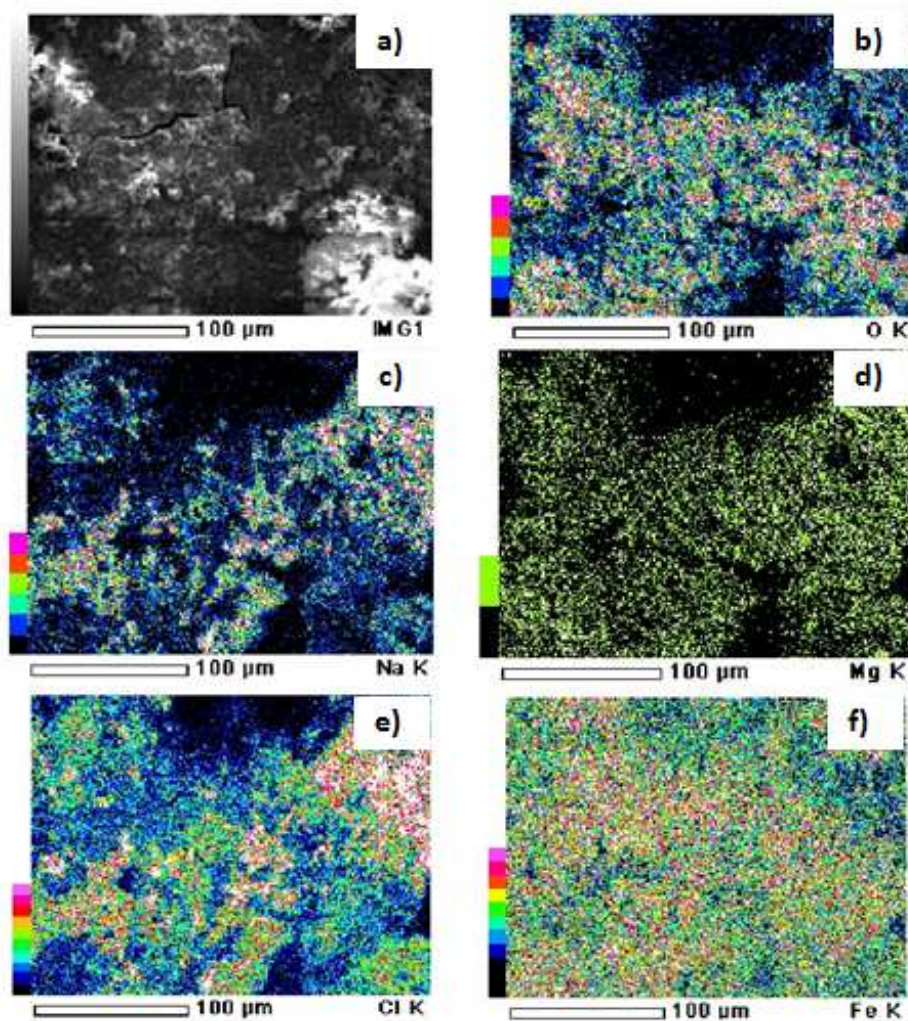


Figure 11 Distribution of elements on corroded steel surface after 1 month of exposure to Tol Mandara solution at ambient temperature. (a) SEM image, (b) O, (c) Na, (d) Mg, (e) Cl, and (g) Fe.

In the previous description, there are no significant differences in magnitude of conductivity, salinity and TDS for all test solutions over all time exposure ranges, except dissolved oxygen. The steel's corrosion rate in all test solutions tended to increase for all time exposure ranges. It is known that seawater parameters such as conductivity, salinity and TDS are relatively unchanged during corrosion testing.

4 Conclusions

The corrosion behavior of mild steel in seawater from the northern coast of Java (Suramadu and Muara Baru) and the southern coast of Bali (Tol Mandara) was evaluated. The corrosion resistance of the mild steel decreased in test solutions with seawater taken from sites in Muara Baru, Suramadu and Tol Mandara after up to 1 month of exposure. Furthermore, corrosion of the mild steel in all test solutions induced dissolved oxygen (DO), where the magnitude of DO decreased in all time exposure ranges. Conductivity, salinity and total dissolved solids were almost of the same magnitude for all time exposure ranges. DO and chloride ions play an essential role in the induction of the corrosion risk of mild steel, indicated by the higher salinity of the solutions from the three natural seawater sites. On the other hand, the decrease of the DO level denotes the presence of a reduction process in all test solutions. The morphology of the corroded mild steel samples tended to be uniform in all test solutions after exposure.

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