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CORROSION BEHAVIOR OF MILD STEEL IN SEAWATER FROM KARANGSONG & ERETAN OF WEST JAVA REGION, INDONESIA

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ABSTRACT

The corrosion behavior of mild carbon steel, has been investigated using an immersion test and energy-dispersive X-ray spectroscopy in solutions from the sites of Karangsong and Eretan, Northern Coast of West Java Region, Indonesia. As reference, solutions of 3.5% and 5% NaCl were prepared. Salinity, conductivity, and total dissolved solids (TDS) were measured. It was found that uniform corrosion observed on mild steel during the immersion test. Corrosion resistance of alloys decreases with increasing exposure time in natural seawater solutions. Since magnitudes of conductivity, salinity and TDS of all test solutions are similar, it implied that chloride ion have primary role for inducing the corrosion risk of mild steel. That parameter hinders the formation of stable passive film on the surface of corroded mild steel.

Key words: *conductivity; immersion test; mild steel; salinity; seawater; total dissolved solids*.

INTRODUCTION

Mild steel has become one of the mostly used materials in the field of engineering all over the world. It is used widely in the construction of roads, railways and in other infrastructures, appliances and buildings (Adetoro Kareem, 2011). These alloys are the most commonly applied as structural materials in various industries due to its good mechanical strength, easy to be manufactured, 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 have been chosen for such applications (Malik *et al.,* 1999).

Moreover, seawater is a complex chemical system which affected by various parameters, including concentration and access of dissolved oxygen (DO), salinity, concentration of minor ions, biological activity, and pollutants (ASM, 1987). The corrosion of mild steel immersed in sea water is influenced mainly by those parameters (Bhosle & Wagh, 1992). Consequently, material specimens of seawater have different corrosivity depend on the sampling location of bulk seawater mass (Jones, 1992). The balance of organisms and dissolved organic nutrients begins to alter as soon as a natural seawater specimen is isolated from the parent water mass. Therefore, natural seawater is not easily simulated in the laboratory for corrosion-testing purposes due to that phenomenon. Hence, solution of 3.5% NaCl is commonly applied for references of simulating sea water.

The other researchers already had investigated the corrosion behavior of mild steel considering the factors of dissolved oxygen, salinity, and temperature in sub-tropical regions (Durodula *et al.,* 2011 ; Al-Moubaraki *et al.,* 2015 ; Temperely, 1965). In southeast region as representative of tropical areas, Wan Nik and co-workers had investigated the corrosion behavior of mild steel in the seawater from Kuala Terengganu Coastal Area, Malaysia (Wan Nik *et al.,* 2011). In addition, our preceding research had also investigated the relationship between the corrosion behavior of steel and those environmental parameters in Bali, Madura and Jakarta Regions, Indonesia (Sundjono *et al.,* 2017). They found the differences on dissolve oxygen and salinity causes the different corrosion behavior of mild steel in the coastal area (Sundjono *et al.,* 2017). However, with regard to mild steel, there is little study on its corrosion behavior in tropical seawater particularly from northern coast of West, Indonesia. Therefore, the objective of the work is to elucidate the corrosion behavior of mild steel in tropical seawater in Indonesia.

Experimental

Sample preparation

The specimens of mild steel were prepared (length of 20 mm, width of 20 mm, and thickness of 1 mm). Prior to the experiments, the removal of corrosion products on the metal specimen was conducted by pickling method according to ASTM G1-81. After that, the pickled specimens were cleaned and washed using distilled water then acetone, and stored in vacuum desiccators. They were weighed for the initial weight. Seawater as corrosive media was taken from different areas i.e. Eretan (A) and Karangsong (B) Regions Northern Java Island, Indonesia as shown in Figure 1. In addition, 3.5% NaCl and 5% NaCl solutions were prepared as reference solutions. The composition of mild steel is shown in Table 1.

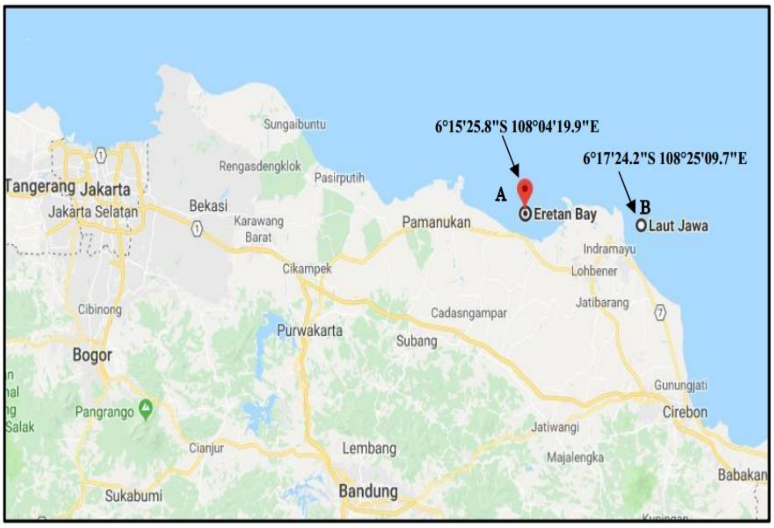

Fig. 1 Various sites of seawater (A dan B).

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

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

Weight Loss Analysis

Before the specimens were cleaned with pickling solutions contain hydrochloride acid (HCl) and hexamethylene tetramine (ASTM Commite G1 1999), the specimens were weighed for the initial weight by using analytical balance (accuracy of 0.0001g). After that, the specimens were immersed in the seawater obtained from Karangsong site and Eretan site. Each specimen was sampling out in certain days interval during 30 days experiment. Before weighing, the specimen was cleaned with distilled water and immersed in pickling solution to remove the corrosion product. The specimen was washed with distilled water, dried and weighed in order to get the final weight.

Generally, carbon steel such as UNS G10400 that applied as immersed offshore infrastructures are attacked by uniform corrosion (Ismail & Adan, 2014). Therefore, the calculation of corrosion rate (CR) is calculated assuming uniform corrosion over all surfaces of the specimens. One of method for the calculation of corrosion rate is weight loss, which its formula used to calculate corrosion rate is as shown in following expression (Afolabi *et al.,* 2014).

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

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

The Measurement of seawater Parameters and the Observation of Corroded Specimens

The main parameters of seawater which is affecting corrosion rate of steel are salinity, pH, and temperature (Paul, 2012). These parameters were considered to in a main part of this work. The seawater parameters were measured using, HQ40d Advanced Portable Meter. This instrument is handheld system for field measurements of salinity, conductivity, temperature; total dissolved solid (TDS) and pH. During the metal immersion experiment, the parameters were measured at certain interval and compared between sites A and B. In addition, the observation for constituent distribution on the surface of corroded specimens was conducted by using energy-dispersive X-ray spectroscopy.

RESULT AND DISCUSSION

The Relation of Weight Loss Analysis and Seawater Parameters

Figure. 2 shows the alteration in corrosion rate of the carbon steel obtained from immersion using seawater from Karangsong and Eretan sites, respectively. Corrosion rate of carbon steel in 3,5%wt and 5%wt NaCl solutions are presented for comparison. The figure shows the immersion time dependence of corrosion rate for carbon steel in different environments. The first phase is the initiation phase which is shown by an increase drastically in corrosion rate at 10 days of exposure. The higher corrosion rate takes place due to the role of oxygen and chloride contents in electrochemical reactions (Sundjono *et al.,* 2017 ; Ismail *et al.,* 2014). Moreover, following the first phase, their corrosion rates decrease until about 21 days of exposure. The decrease in corrosion rate can be related to the formation of passive film on the surface of carbon steel which behaves a protective layer from a further corrosion process (Gaius Debi Eyu *et al.,* 2016). However, the corrosion rates increase slightly up to the 30 days of exposure in both reference solutions, but not in the solutions from Karangsong and Eretan sites. On the other hand, the higher corrosion rate of carbon steel was observed in Karangsong solution compared with Eretan solutions in first phase, where the same magnitude of corrosion rates took place up to 30 days exposure. Chloride anions in the NaCl solution can remove the metal cations accumulated on the anode by forming soluble compounds, which increases electrochemical reaction and corrosion rates significantly on steel (Mousa May, 2016). In our preceding results, the main role of oxygen also contribute to increase corrosion rate in first phase and to compose passive layer on steel surface, however, the detrimental effect of chloride can breakdown passive layer of steel (Sundjono *et al.,* 2017). Even though, the highest concentration of seawater is chloride compounds, calcium carbonate and magnesium hydroxide has a certain beneficial effect to decrease corrosion rate as a precipitation on metal surface (Xiangyu Hou *et al.,* 2017). Therefore, it implies that the detrimental effect in NaCl solution can be suppressed in corrosion rate with the presences of other compounds in seawater but not in both references solutions.

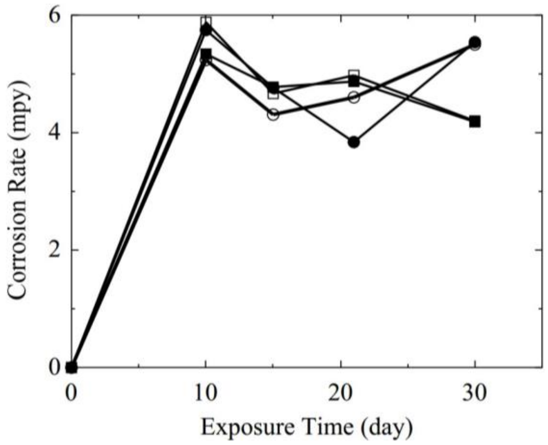

Fig. 2 Corrosion rate of mild steel as function of exposure time in the solutions containing ○ 3.5% NaCl ; ● 5% NaCl ; □ seawater of Karangsong site and ■ seawater of Eretan site.

Figure 3 shows salinity level as function of exposure time in different solutions at the ambient temperature. However, the salinity of 5% NaCl could not be detected due to out of the salinity measurement range of HQ40d Advanced Portable Meter. The salinity of seawater of Karangsong and Eretan Regions is similiar, meanwhile 3.5% NaCl solution is lower. However, Salinity is evaluated by determination of $[Cl^-]$ ion concentrations in water, which empirically states that salinity equals 1.80655 × $[Cl^-]$ (Zakowski et al.2014). To be noted, The Cl^- ion in the seawater is correlated mainly to the content of NaCl, $MgCl_2$ and KCl (Martin, 2016).

Therefore, seawater for Karangsong and Eretan sites have higher salinity compared with 3.5% NaCl solution. Higher the salinity means lower the oxygen solubility, where the increase of dissolved oxygen can increase corrosion risk. In Figure 2, the corrosion rate of steel in different seawater sites is higher than that in 3.5% NaCl solution up to 21 days exposure, but not up to 30 days. In addition, on the basis of the results, the magnitude of salinity in different seawater sites is almost the same at various exposure times. However, it implies that corrosion risk of steels in all test solutions was depended on the same magnitude of salinity up to 21 days exposure, but not up to 30 days in natural seawater solutions.

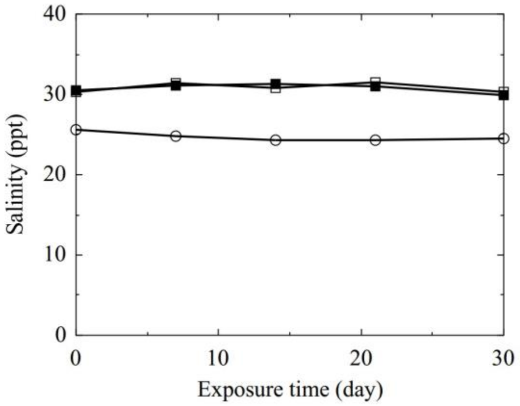

Fig 3. Salinity level as function of exposure time in the solutions containing ○ 3.5% NaCl ; □ seawater of Karangsong site and ■ seawater of Eretan site.

In practice, conductivity measurements are carried out. Water electrical conductivity (EC) is usually used as a salinity indicator. The presence of dissolved salts in water is related to the value of its EC, as they provide electrical charges interacting as ions in movement (Héctor Peinado-Guevara et al. 2012). Figure 4 shows electrical conductivity as function of exposure time in various solutions at ambient temperature. According to the results, the conductivity of seawater from different sites is almost the same level, which compared to the NaCl reference solutions. The highest conductivity of 5% NaCl solution shows high total quantity of dissolved salt ions but not in the lowest that of 3.5% NaCl solution. In addition, the conductity of all test solutions is almost same magnitude in all period of exposures. Furthermore, the same magnitude of conductivity in different seawater sites correlated to the same concentration of dissolved ions or total dissolved various salts. The corrosion rates of metal tend to increase when water electrical conductivity increases (Zakowski *et al.,* 2014). However, the present results shows that corrosion rates of steel in reference solutions tend to increase up to 30 days of exposure but no change of conductivity levels in the solutions. Meanwhile, the corrosion rates in seawater sites decrease up to 30 days of exposure. It was concluded that corrosion risk of steel is not depended on the conductivity in all test solutions for all time exposures.

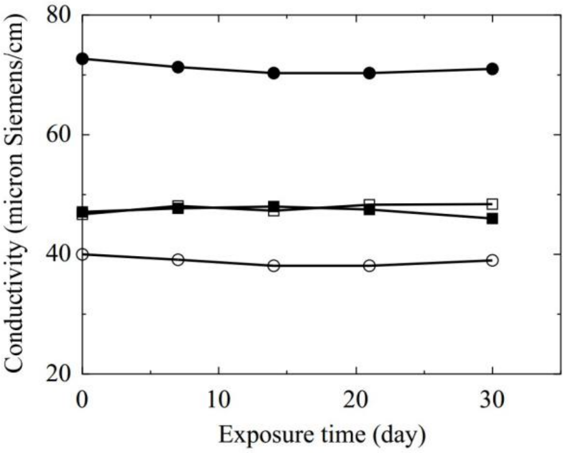

Fig. 4 Conductivity as function of exposure time in the solutions containing ○ 3.5% NaCl; ● 5% NaCl; □ seawater of Karangsong site and ■ seawater of Eretan site.

Figure 5 shows total dissolved solids (TDS) as function of exposure time in the test solutions. The TDS parameter quantifies both inorganic and organic compounds in the ionic, particle or colloidal states (Boerlage 2012). Water can be regarded as fresh (TDS < 1,500 ppm), brackish (1,500 ppm < TDS < 5,000 ppm) or saline (TDS >5,000 ppm) (Zakowski et al. 2014). All test solutions were categorized as saline solutions due to above 5 g/L (5000 ppm). The measurement of TDS refers to conductivity, which is the following expressed in the following equation,

TDS (ppm) = Conductivity (μS/cm) x conversion factor (Al Dahaan *et al.,* 2016).

where HQ40d Advanced Portable Meter used conversion factor around 0.64. Therefore, the value of TDS is directly proportional to that of conductivity. In the relation of corrosion rates of steel, high levels of TDS increase corrosion risk. Furthermore, according to the results, TDS in different seawater sites is almost the same magnitude compared to reference salt solutions. The highest TDS of 5% NaCl solution shows high total quantity of dissolved salt ions but not in the lowest that of 3.5% NaCl solution. In addition, TDS of all test solutions is almost same levels in all period of exposures. However, the results of corrosion rates of steel in reference solutions tend to increase up to 30 days of exposure but no change of TDS levels in the solutions. The corrosion rates in seawater sites go down up to 30 days of exposure. It was concluded that corrosion risk of steel is not depended on TDS factor in all test solutions for all time exposures.

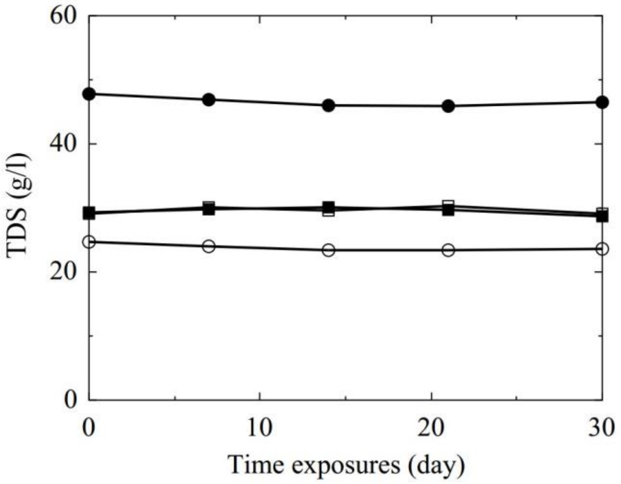

Fig.5 Total dissolved solids (TDS) as function of exposure time in the solutions containing ○ 3.5% NaCl; ● 5% NaCl ; □ seawater of Karangsong site and ■ seawater of Eretan site.

Element Distribution of Corroded Surface after Exposure

Figure 6 shows distribution of elements on surface of corroded steel of Karangsong solution after 30 days exposure. The major element of Fe was spread over the surface uniformly. The present of elements such as Na, Ca, S, Mg and Cl indicated from the constituent of seawater such as NaCl,$CaCl_2$, $CaSO_4$ and $MgCl_2$ (Ravisankar *et al.,* 1988 ; Shengxi and Hihara, 2014). The high concentration of oxygen which distribute over the surface of steel indicates the presence of corrosion product of oxide film. Furthermore, the Cl was observed over the surface. It implies that there is corrosion product containing metastable salt oxide product on the surface.

Figure 7 shows the surface distribution of elements for carbon steel after exposure of Eretan solution. The major constituent of Fe was distributed over the surface uniformly, where the component of salt compounds are Na, Mg, Ca, S and Cl from seawater. The presence of Ca and Mg cations was indicated from the compound of $CaCl_2$ and $MgCl_2$ in seawater (Shengxi and Hihara 2014). Moreover, the presence of oxygen was covered on the surface, which exhibit corrosion product of oxide film. In addition, the tendency of higher corrosion rate of steel up to 30 days of exposure denotes the essential role of Cl ion as detrimental ion of oxide film breakdown. Furthermore, all morphologies of corroded surface on mild steel were uniform predominantly in all seawater solutions after exposures.

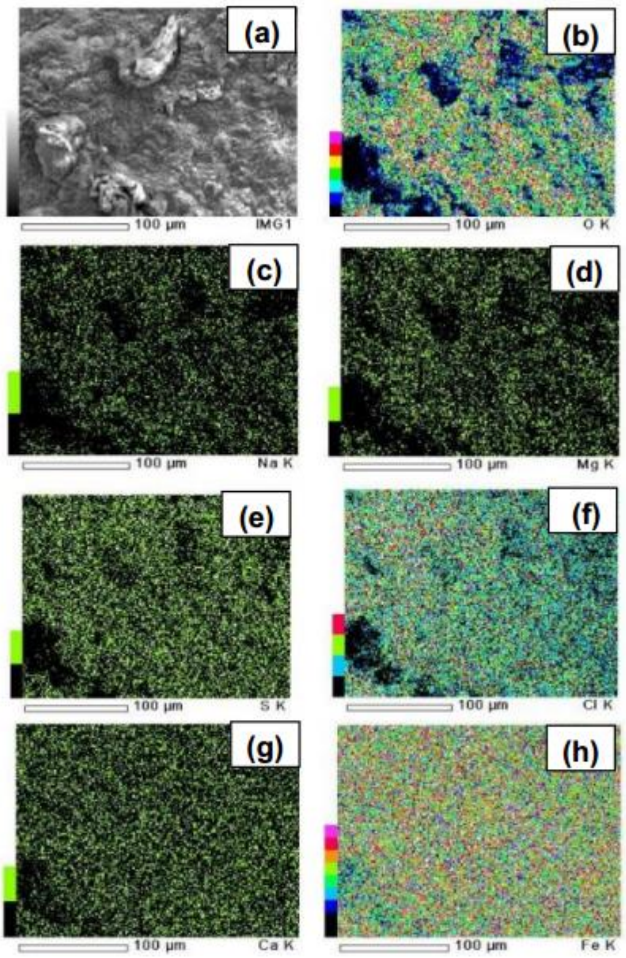

Fig. 6 Distribution of elements on corroded surface steel after 30 days of exposure of Karangsong solution at ambient temperature. (a) SEM Image, (b) O, (c) Na, (d) Mg, (e) S, (f) Cl, (g) Ca and (h) Fe.

On the previous description, there are no different significance magnitudes of conductivity, salinity and TDS for all test solutions all range of time exposure. The corrosion rate of steel in all test solutions tends to increase for all range of time exposure. It is known that seawater parameters such as conductivity, salinity and TDS are relatively stable during corrosion test. Our preceding results showed the surface distribution of elements of carbon steel samples after exposed to 3.5% and 5% NaCl solutions, respectively, where the presence of oxygen and chloride were spread over the surface uniformly (Sundjono et al. 2017).The presence of oxygen indicated that the surfaces were covered by ferrous oxide film. On the other hand, the presence of element of Cl which lies on the surface indicated the presence of salt film.

In the presence of aggressive chloride ions, the outer layers of passive oxide films are displaced due to catalytic Fe^{3+} formation, where the two steps reaction took place with intermediate metastable FeOCl film displaced to Chloride Island on passive surface (Popov, 2015). It means that the salt island (FeOCl) was loosely adhere to the steel surface, thus cannot protect it from further corrosion attack. The FeOCl acts as potential active site (anodic site), which film breakdown take place and dissolve the steel (Popov, 2015).

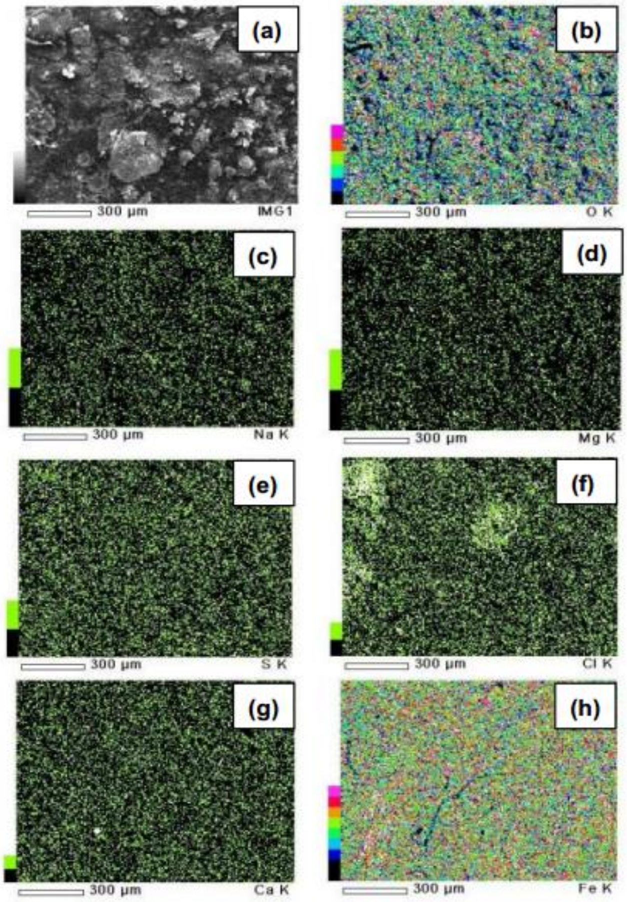

Fig 7. Distribution of elements on corroded surface steel after 30 days of exposure of Eretan solution at ambient temperature. (a) SEM Image, (b) O, (c) Na, (d) Mg, (e) S, (f) Cl, (g) Ca and (h) Fe.

CONCLUSIONS

Corrosion behavior of mild steel in seawater from Northern Coast of West Java Region has been evaluated. The corrosion resistance of carbon steels decrease in test solutions from Karangsong and Eretan sites up to 30 days of exposure. Conductivity, salinity and total dissolved solids are almost the same magnitude in all range of time exposure. The chloride ion have a essential role for inducing the corrosion risk of mild steel, which indicated the higher salinity of solutions from two natural seawater sites. The morphology of corroded mild steels tends to be uniform in natural seawater after exposure.

CONFLICTS OF INTEREST

The authors declare no conflict of interest

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REFERENCES

Adetoro Kareem. (2011). Effect of Environment on the Mechanical Properties of Mild Steel. *ARPN Journal of Science and Technology*, *3*(9), 915-918

Afolabi,A.S., Muhirwa,A.C., Abdulkareem, A.S., & Muzenda,E. (2014). Weight Loss and Microstructural Studies of Stressed Mild Steel in Apple Juice, Int. *J. Electrochem. Sci. 9*, 5895 – 5906

Al Dahaan, S., Al-Ansari, N., & Knutsson, S. (2016). Influence of Groundwater Hypothetical Salts on Electrical Conductivity Total Dissolved Solids. *Engineering*, *8*(11), 823-830.

Al-Moubaraki, A.H., Al-Judaibi,A., & Asiri,M. (2015). Corrosion of C-Steel in the Red Sea: Effect of Immersion Time and Inhibitor Concentration, Int. *J. Electrochem. Sci., 10*, 4252 – 4278

ASTM Committee G1. (1999). Standard Practice for Preparing, Cleaning, and Evaluating Corrosion Test Specimens. *Book of ASTM Standards*, *G01-05*, 15-21

ASM. (1987). *ASM Metals Handbook*, Vol. 13: Corrosion, 9th. ed., ASM International

Bhosle,N.B, & Wagh, A.B. (1992). The effect of organic matter associated with the corrosion products on the corrosion of mild steel in the Arabian sea. *Corrosion Science, 33*(5), 647-655

Boerlage, S. F. E. (2012). Measuring salinity and TDS of seawater and brine for process and environmental monitoring—which one, when? *Desalination and Water Treatment, 42*(1–3), 222–230

Durodola, B.M., Olugbuyiro, J.A.O., Moshood, S.A., Fayomi,O.S, & Popoola, A.P.I. (2011). Study of Influence of Zinc Plated Mild Steel Deterioration in Seawater Environment. Int. *J. Electrochem. Sci, 6*, 5605 – 5616

Eyu, G. D., Will, G., Dekkers, W., & MacLeod, J. (2016). Effect of dissolved oxygen and immersion time on the corrosion behaviour of mild steel in bicarbonate/chloride solution. *Materials*, *9*(9), 748.

Héctor Peinado-Guevara, Carlos Green-Ruíz, Jaime Herrera-Barrientos, Oscar Escolero-Fuentes, Omar Delgado-Rodríguez, Salvador Belmonte Jiménez, and María Ladrón de Guevara. (2012). Relationship between chloride concentration and electrical conductivity in groundwater and its estimation from vertical electrical soundings (VESs) in Guasave, Sinaloa, Mexico, Cien. *Inv. Agr, 39*(1), 229-239

Ismail,A. & Adan,N.H. (2014). Effect of Oxygen Concentration on Corrosion Rate of Carbon Steel in Seawater, American *Journal of Engineering Research*, *3*(1), 64-67.

Jones, D.A. (1992). *Principles and Prevention of CORROSION*. Macmilan Publishing Company

Malik, A. U., Ahmad, S., Andijani, I., & Al-Fouzan, S. (1999). Corrosion behavior of steels in Gulf seawater environment. *Desalination*, *123*(2-3), 205-213.

Martin,M.M. (2016*). Industrial Chemical Process Analysis and Design*, Elsevier.

Mousa May. (2016). Corrosion behavior of mild steel immersed in different concentrations of NaCl solutions, *Journal of Sebha University-(Pure and Applied Sciences), 15*(1), 1-12

Paul, S. (2012). Modeling to Study the Effect of Environmental Parameters on Corrosion of Mild Steel in Seawater Using Neural Network, *ISRN Metallurgy*, *2012*, 1-6

Popov, B.N. (2015). Corrosion Engineering: Principles and Solved Problems, Elsevier

Shengxi Li and L. H. Hihara (2014) Aerosol Salt Particle Deposition on Metals Exposed to Marine Environments: A Study Related to Marine Atmospheric Corrosion, *Journal of The Electrochemical Society, 161*(5), C268-C275

Ravisankar, M., Reghunath, A.T., Sathianandan, K & Nampoori,V.P.N. (1988). Effect of dissolved NaCl, $MgCl_2$, and Na_2SO_4 in seawater on the optical attenuation in the region from 430 to 630 nm, *Applied Optics*, *27*(18), 176-188

Sundjono, Gadang Priyotomo, Lutviasari Nuraini & Siska Prifiharni. (2017). Corrosion Behavior of Mild Steel in Seawater from Northern Coast of Java and Southern Coast of Bali, Indonesia *J. Eng. Technol. Sci., 49*(6), 770-784

Temperley, T. G. (1965). Corrosion phenomena in the coastal areas of the Persian Gulf. *Corrosion Science*, *5*(8), 581-589.

Xiangyu Hou, Lili Gao, Zhendong Cui and Jianhua Yin. (2017). Corrosion and Protection of Metal in the Seawater Desalination, *IOP Conf. Ser. Earth Environ*. *Sci., 108*, 1-4

Wan Nik, W.B.Z., Rahman, F.M.M., & Rosliza, R. (2011). Corrosion Behavior of Mild Steel in Seawater from Two Different Sites of Kuala Terengganu Coastal Area, *International Journal of Basic & Applied Sciences IJBAS-IJENS, 11*(6), 75-80

Zakowski, K., Narozny, M., Szocinski, M., & Darowicki, K. (2014). Influence of water salinity on corrosion risk—the case of the southern Baltic Sea coast. *Environmental monitoring and assessment*, *186*(8), 4871-4879.