

CORROSION COMPARISON OF GALVANIZED STEEL AND ALUMINUM IN AQUEOUS ENVIRONMENTS

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ABSTRACT

A corrosion test of galvanized steel and aluminum was carried out in three different aqueous environments, 5% NaCl solution, sea water and rain water, using the immersion test technique. Corrosion rate was measured in mdd ($\text{mg}/\text{dm}^2/\text{day}$) units. Aluminum was considered as a possible alternative to galvanized steel. The corrosion characteristics of the corroded samples were investigated by XRD, XRF and SEM analysis. Although various results were obtained all through this study, aluminum was seen as more corrosion resistant than galvanized steel in the conditions tested in all three aqueous environments. Galvanized steel might be more corrosion resistant than aluminum in long term exposure in rain water. Without taking into account cost comparisons, aluminum can be used as a substitute for galvanized steel in industrial structures (roofing sheets) and water distribution systems.

Key words: Corrosion rate (mdd), galvanized steel, aluminum, aqueous environment.

INTRODUCTION

Metals are very important engineering materials, but the most serious drawback to their mechanical and electrical properties is corrosion. This has a huge economic and environmental impact on virtually all facets of the world's infrastructure, from highways, bridges and buildings, to oil and gas, chemical processing and water and wastewater systems. In addition to causing severe damage and threatening public safety, corrosion disrupts regular operations and requires the extensive repair and replacement of failed assets. Corrosion can only be reduced, however, it cannot be prevented because thermodynamically it is a spontaneous phenomenon. Depending on environment, the corrosion of a particular material can be fast or slow. Sensitized 18-8 stainless steel, for example, is severely attacked in hours by polythionic acid (Syed, 2006). Although the famous iron Delhi Pillar in India was made almost 2000 years ago, and is almost as good as new, it should be noted that it has been exposed to mostly arid conditions (Fontana, 1987). Attempting to reduce corrosion is vital for better industrial production, public safety, avoiding health hazards etc.

Galvanized steel is used in aqueous environments in many indoor and outdoor applications where rust resistance is needed. It is used in applications such as underground pipelines, under sea water, frames to build houses, and many household appliances, automotive body parts, telecommunication industry, power transmission lines, thermal power plant etc. (Lin, Lu, & Kong, 2008; Sherif, Almajid, Bairamov, &

Al-Zahrani, 2012). The protection obtained by zinc (Zn) coating is due to the barrier and galvanic double protective effect (Bajat, Stanković, Jokić, & Stevanović, 2010; Kartsonakis, Balaskas, Koumoulos, Charitidis, & Kordas, 2012). Atmospheric corrosion of galvanized steel structures begins through an electrochemical process when the Zn surface becomes wet with rain, mist, or dew (Nriagu, 1978). The American Galvanizers Association (AGA) conducted tests of the corrosion of galvanized steel in water collected from marine environments all over the USA and found that soft water, tropical sea water, and high oxygen content causes higher corrosion in zinc coating of galvanized steel (American Galvanizers Association).

Aluminum (Al) is one of the most abundant elements in nature. Its low density, high elastic modulus, thermal and electrical conductivity, corrosion resistance and its capacity to form alloys with many elements makes it one of the most useful materials in construction (Hatch, 1984). Al is used in buildings for a wide spectrum of applications, including plumbing products and replacement windows. The corrosion of Al has mainly been investigated through field studies (Graedel, 1989). Few laboratory investigations in controlled environments have been published. In one study, it was found that Al has very low resistance to a corrosive environment (3%NaCl) in a static regime, and corrosion processes take place on the Al surface (Hagioglu, Gheorghies, Cantaragiu, & Moisa, 2010). In another study, the effect of rain on Al alloy and galvanized steel roofing sheets, as well as their relative corrosion resistance, was studied (Abdulkarim, Abdullahi, & Salam, 2009). The corrosion behavior of pure Al after different immersion intervals in 3.5% NaCl solutions was also studied, and it appeared that the corrosion rate of Al decreased with increasing immersion time due to the growing thickness of the corrosion product (Sherif, Almajid, Latif, & Junaedi, 2011)

In Bangladesh, roofing systems in most houses in rural areas and some houses in urban areas involve galvanized steel sheets. There is little use of Al as roofing sheets, but the application of Al as window frames has recently been increasing. Similarity in applications both for galvanized steel and Al put them in similar environments like saline water, humid atmosphere, rain, weather and so on. Corrosion is the major, and a common challenge to these materials. Although much study has been independently conducted on the corrosion of galvanized steel and Al in various environments, corrosion study of these two materials in common environments are rare. This work makes a comparative study of corrosion behavior of galvanized steel and Al in three aqueous environments, 5% NaCl solution, sea water and rain water. Aqueous environments are chosen as the corroding media because in real case scenarios the substrates come in contact with liquid and gases such as chemical processing plants, plumbing applications, oil rigs, offshore petroleum pipelines, household appliances, roofing sheets, machine parts, marine structures etc.

EXPERIMENTAL DETAILS

Galvanized steel sheets and Al sheets of 4.5×2.0 cm in size were taken as substrates. All substrates were cut from the main sheet by a hand shear cutting machine. The thickness of both substrates was 0.5mm. The area (A in dm^2) of all the substrates was measured using slide calipers. A schematic of the sample geometry is shown in Figure 1(a). All the substrates were cleaned with detergent, washed with acetone and dried. The initial weight (w_i in mg) of all the substrates was measured using an electronic weighing balance. All parameters were measured at ambient temperature. A 5% NaCl solution was prepared using deionized water and reagent grade NaCl salt; sea

water was collected from the Bay of Bengal in the Chittagong area; and rain water was collected during rain in Dhaka city. All substrates were then immersed in liquid environments (5% NaCl solution, sea water and rain water). For each environment, five samples were dipped in beakers containing the liquid and kept there for T days (T = 1, 2, 3, 4 and 5 respectively). The experimental set up for corrosion test by immersion is shown in Figure 1(b). All the substrates were then cleaned again with detergent, washed with acetone and dried. Final weights (w_f in mg) were measured for all substrates. A flow chart of the experimental procedure for the corrosion test is shown in Figure 2.

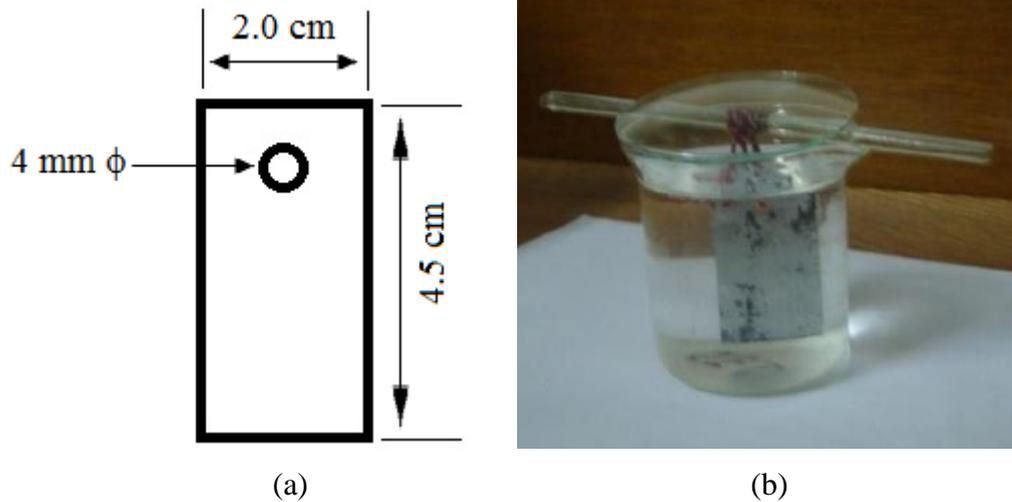


Figure 1. (a) Schematic geometry of sample and (b) experimental set up of corrosion test by immersion technique.

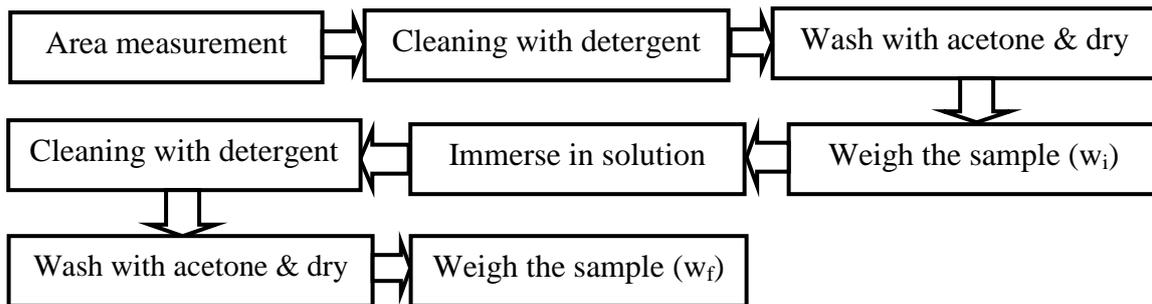


Figure 2. Flow chart of the experimental procedure for corrosion test by immersion.

Corrosion rate in mdd ($\text{mg}/\text{dm}^2/\text{day}$) unit was measured by using the following formula:

$$\text{Corrosion rate} = \frac{w_i - w_f}{T \times A}$$

Where, w_i = initial weight of sample in mg
 w_f = final weight of sample in mg
 T = immersion time in day
 A = Area of sample in dm^2

Corroded surface characteristics were investigated using XRD (X-ray diffractometer), and XRF (x-ray fluorescence). Scanning electron microscopy (SEM) was then

employed to inspect the surface morphology of the bare substrates and corroded samples.

RESULTS AND DISCUSSION

Corrosion in Aqueous Environments

The change in corrosion rate with exposure time for galvanized steel and Al in various environments is shown in Figure 3. A varied corrosion rate with exposure time both for galvanized steel and Al was observed in various environments. For example, the corrosion rate decreases and increases with an increase of exposure time in 5% NaCl solution and sea water respectively for both the substrates. A decreasing trend in the corrosion rate was observed for galvanized steel in rain water which is in contrast to Al which showed an increasing corrosion rate with exposure time. Within these diverse patterns, the only replicable result was that the corrosion rate for galvanized steel is higher than that of Al for every test condition. The diverse corrosion behavior in various environments is discussed separately in the following paragraphs.

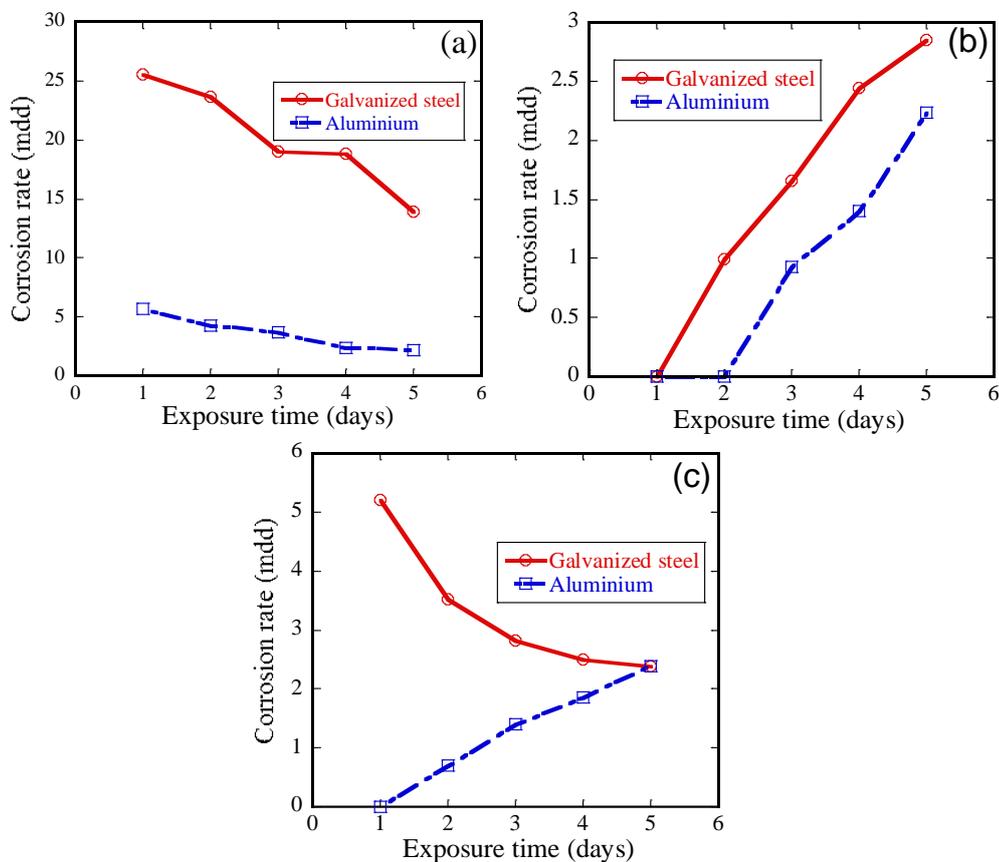


Figure 3. Corrosion rate as a function of the exposure time of galvanized steel and Al under immersion test in (a) 5% NaCl solution, (b) sea water and (c) rain water.
 (a) Corrosive environment: 5% NaCl solution

Both galvanized steel and Al immersed in 5% NaCl solution showed decreasing corrosion rates with increasing exposure time (Figure 3(a)). The value of corrosion rates in mdd for the Al sample in 5% NaCl environment was much lower than for galvanized

steel. Chlorides are severely corrosive to Zn (American Galvanizers Association), so initially the corrosion rate was high. As most of the Zn corrodes early, decreasing the chloride concentration in an NaCl environment with time, corrosion rate decreases with increasing exposure time. Surface analyses of corroded samples by XRF test are shown in Table 1. A galvanized steel sample surface after corrosion in 5% NaCl solution contains 47.14% Zn and 32.25% Fe which indicates major corrosion of the sample. The appearance of this corroded sample is shown in Figure 4. A small fraction of the entire sample surface is seen covered by Zn coating. The non-adherent corrosion products found in the beaker bottom are $ZnCl_2$ (white crystalline powder or granule). In the XRD pattern, Zn and chloride peaks are found (Figure 5(a)). Moderate Al corrosion is supposed to be occurred in 5% NaCl solution exposing 62% Al and 36.71% O_2 as seen in the XRF test. Dissolved O_2 and CO_2 in distilled water are believed to form protective a film of aluminum oxide to resist further corrosion (Sherif et al., 2011) resulting in much less corrosion of Al in 5% NaCl solution compared to galvanized steel.

b) Corrosive environment: sea water

Sea water is high in salt content in the form of various chlorides and often the presence of sulfide is detrimental (Jayaraman, 1951). It is a good electrolyte and corrosion is affected by oxygen content, temperature and biological organism (Al-Fozan & Malik, 2005). It also contains carbonates which form a protective film on a Zn (American Galvanizers Association) as well as on an Al surface (Wan Nik, Sulaiman, Fadhli, & Rosliza, 2010). The corrosion rate in sea water is thus much less than in 5% NaCl solution for both the samples. The corrosion rate gradually increases with increasing exposure time (Figure 3(b)). Although the corrosion curve in sea water shows an increasing trend, the absolute value in mdd is much lower than in 5% NaCl solution as seen through the Y-axis scale. The presence of Ca and Mg ions also inhibit corrosion in sea water because they form a protective film of carbonates (American Galvanizers Association).

Table 1. XRF data of samples after corrosion.

Sample	Corrosion environment	Elements	Mass (%)	Remarks
Galvanized steel	5% NaCl solution	Zn	47.14	Much Zn corrosion
		Fe	32.25	
	Sea water	Zn	82.43	Less Zn corrosion
		Fe	14.13	
	Rain water	Zn	77.01	Moderate Zn corrosion
		Fe	12.33	
Al	5% NaCl solution	Al	61.99	Moderate Al corrosion
		O	36.71	
	Sea water	Al	85.23	Less Al corrosion
		O	13.58	
	Rain water	Al	98.8	Negligible Al corrosion
		O	Nil	

The presence of 82.43% Zn in the XRF test (Table 1) on the corroded galvanized steel sheet in sea water ensures a lesser amount of Zn surface corrosion than in the 5%

NaCl solution. This is further supported by only 14.13% Fe exposure of galvanized steel in the sea water corrosion test. An almost linear increase of Al corrosion rate is observed in sea water (Figure 3(b)). XRF data (Table 1) indicates Al and oxygen contents are 85.23% and 13.58% respectively. Graedel (1989) reported that enhanced corrosion occurs in marine environments. Wilkinson and Patterson (1941) investigated the effect of NaCl particles on the corrosion of Al at 293 K. The weight change due to NaCl particles was linear with time. Sanyal and Bhandwar (1962) also reported similar results in their investigation of the effect of NaCl particles on the corrosion of Al at 313 K.

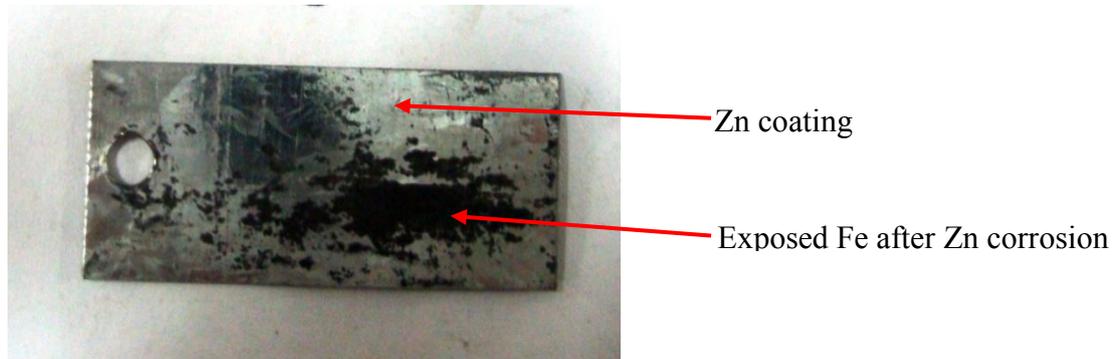


Figure 4. Photograph of galvanized steel sample after corrosion.

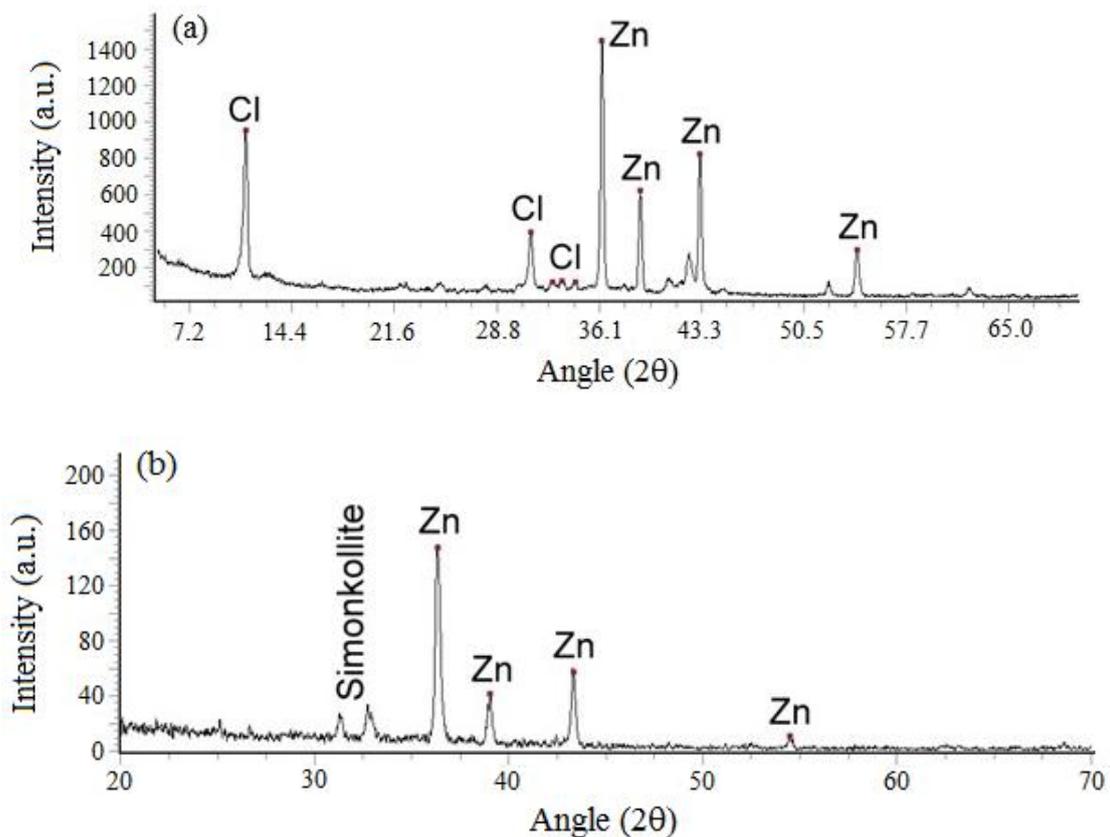


Figure 5. XRD pattern of galvanized steel after five days immersion in (a) 5% NaCl solution, (b) rain water.

(c) Corrosive environment: rain water

Rain water causes higher corrosion than sea water. Rain water falls through the atmosphere so it collects oxygen gas which increases the corrosion rate. Rain water was collected from Dhaka city. As the pollution is high in Dhaka city, the rain water is acidic in nature (Abdulkarim et al., 2009), and thus the corrosion rate is high. In the case of galvanized steel initially the amount of reactants was high but with increasing exposure time this amount decreased resulting in inhibition of the corrosion rate (Figure 3(c)). The XRD test revealed several peaks of Zn (Figure 5(b)). The XRD pattern shows deviations because of the formation of an amorphous phase on the surface. The amorphous phase is Simonkollite [$Zn_5(OH)_8Cl_2 \cdot H_2O$]. The XRF test (Table 1) revealed 77.01% Zn on steel substrate indicating more Zn corrosion than for sea water. When the Zn surface becomes wet with rain, an electrochemical process begins, resulting in corrosion of galvanized steel (Nriagu, 1978). A film of basic zinc carbonate, $2ZnCO_3 \cdot 3Zn(OH)_2$, forms on galvanized steel structures in long exposures (Flinn, Cramer, Carter, Hurwitz, & Linstrom, 1986). This film tends to inhibit further Zn corrosion resulting in a decrease of the corrosion rate with exposure time. However, there are environmental conditions in which film removal processes compete with film formation. In the case of Al, the corrosion rate increases (Figure 3(c)) but the mdd values are very small. XRD shows only an Al peak and XRF indicates less Al deterioration (Al is 98.8% in the corroded sample) (Table 1). It is generally agreed that deposition of SO_2 , and chlorides and the pH in rain water are major factors that determine the corrosion rate of Al. In the presence of SO_2 , oxidizing agents such as O_3 and H_2O_2 may also play a role in the corrosion of Al (Graedel, 1989). Compared to galvanized steel, Al corrodes rather slowly in rain water, because it forms an insulating amorphous oxide film of low solubility in air and aqueous solutions over the pH range from 4 to 8.6 (Syed, 2006). The corrosion rate in mdd for both galvanized steel and Al equalized after five days of exposure. The corrosion rate of galvanized steel tends to decrease whereas that of Al shows an increasing trend. This suggests that galvanized steel might be of superior corrosion resistance compared to Al after five days exposure in rain water.

Surface Morphology of Corroded Sample

SEM images of galvanized steel samples are shown in Figure 6. The samples were exposed for five days in corrosive environments. The SEM image of the unetched substrate sample shows an almost uniform surface (Figure 6(a)) before the corrosion test. Differences in surface elevation are visible as the sample surface is not polished. The sample in 5% NaCl solution corrosion test shows some white corrosion product, or nodules, which are randomly arranged over the corroded surface, and also shows a separate layer on the surface. A sample corroded in sea water reveals a few white nodules attached to the sample surface. The sample of rain water shows a cavity, and some corrosion products or nodules (Figure 6(d)). These are small in number and randomly oriented over the surface. Thus major corrosion products appear on the sample tested in 5% NaCl solution. This morphology is consistent with the corrosion measurement result found in Figure 3. SEM images of Al samples are shown in Figure 7. These samples were also exposed for five days in a corrosive environment. The SEM image of the unetched base sample shows almost uniform surface (Figure 7(a)).

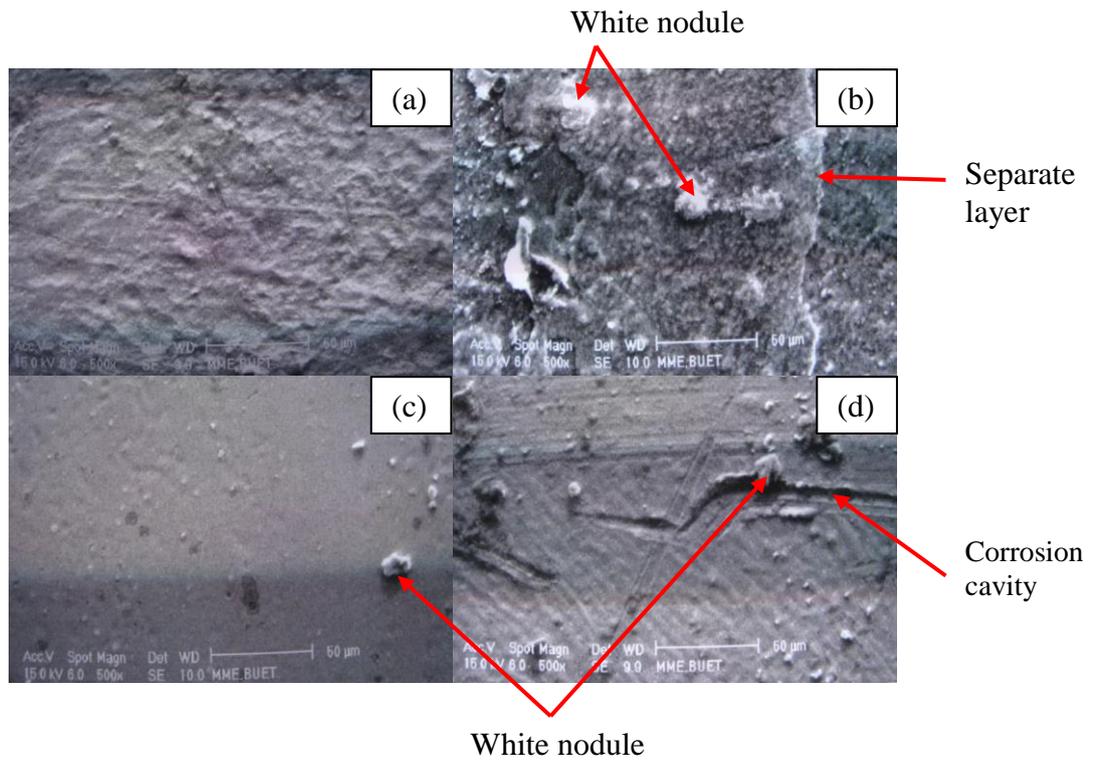


Figure 6. SEM of galvanized steel (a) before corrosion; after corrosion in (b) 5% NaCl solution; (c) sea water and (d) rain water. All corrosion tests were continued for 5 days.

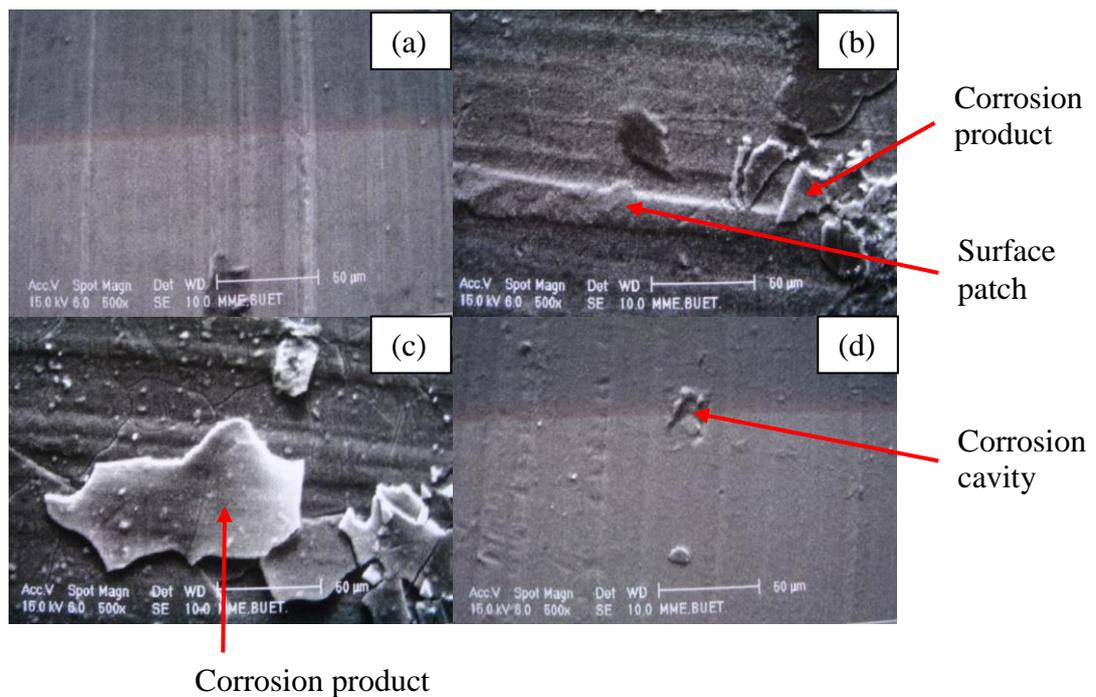


Figure 7. SEM of Al (a) before corrosion; after corrosion in (b) 5% NaCl solution; (c) sea water and (d) rain water. All corrosion tests were continued for 5 days

The SEM image of the Al sample corroded in 5% NaCl solution shows corrosion product embedding on the surface which inhibits further corrosion of the Al

sample in this environment. A longitudinal surface patch is also observed along with the corrosion product (Figure 7(b)). The sample in sea water shows generation of large corrosion products which forced the layer apart sometime after the corrosion commenced (Figure 7(c)). The corrosion products might be basic aluminum sulfates and amorphous aluminum sulfate hydrate under these conditions (Barton, 1976; Graedel, 1989), because in addition to chlorides, sea water contains sulfide salts (Jayaraman, 1951). Identification of the corrosion products would be confirmed by Energy Dispersive X-ray (EDX) and XRD analyses exactly over the products. Stress developed during corrosion is believed to be responsible for corrosion product removal. Corrosion product wedging action causes the propagation of exfoliation attack (Fontana, 1967) which increases the corrosion rate as time passes, i.e. exposure time increases. A consistent corrosion rate data is seen in Figure 3(b). Corrosion in rain water produced cavities on the surface.

CONCLUSIONS

A corrosion test of galvanized steel and Al was conducted in 5% NaCl solution, sea water and rain water. Compositional variation, corroded surface characteristics and surface morphology were studied. Based on the experimental results and analysis, the following conclusions have been drawn:

- a) Varied results were obtained for both galvanized steel and Al. Corrosion rate decreases with increase of exposure time in a 5% NaCl solution both for Al and galvanized steel. In comparison, an increasing trend in corrosion rate is observed for both the samples in sea water. The result in rain water is seen to be decreasing and increasing for galvanized steel and Al respectively.
- b) The highest corrosion rate for galvanized steel (25.59 mdd) is found in a 5% NaCl environment whereas no corrosion occurred in sea water after one day of exposure.
- c) The highest corrosion rate for Al (5.71 mdd) is found in a 5% NaCl environment whereas no corrosion is seen in either sea water or rain water environments after two days and one day of exposure respectively.
- d) Al is proved to be more corrosion resistant in all three environments under the test conditions performed in this study. For long term exposure in rain water, galvanized steel might be more corrosion resistant than Al.

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