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Corrosion of Galvanized Steel and its Substitutes in Various Environments

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Abstract

Corrosion test of galvanized steel has been carried out in three different aqueous environments (NaCl solution, sea water and rain water) by weight loss measurement technique by exposing them from one to five days in the selected environment. Corrosion rate is measured in mdd (milligram/decimeter^2*/day) units. Aluminium and copper is considered as a possible alternative of galvanized steel. Aluminium and copper is treated in same manner for substitution of galvanized steel. Corrosion characteristics of the corroded samples are also investigated by XRD, XRF and SEM analysis to understand the corroded surface morphologies. Copper is better than galvanized steel in NaCl and rain water environments. On the contrary, Aluminium can be easily used as a substitute material for galvanized steel in industrial structure (Roofing sheets) and water distribution system considering all these aqueous environment. Aluminium is better corrosion resistant than galvanized steel in liquid environments. So, aluminium can use as a substitute material for galvanized steel in industrial structure (Roofing sheets) and water distribution system considering these entire aqueous environments.*

Key words: *Corrosion rate (mdd), NaCl solution, Sea water, rain water.*

1. Introduction

Galvanized steel is used in aqueous environments in many indoor and outdoor applications. Galvanized steel is widely used in applications where rust resistance is needed. Galvanized steel is also used in underground pipeline under sea water, frames to build houses and several household appliances. On the contrary, aluminium is used in buildings for a wide spectrum of applications, rainwater goods and replacement windows. Copper tube is the highest quality material available today for a variety of building applications including plumbing, fire sprinklers and harsh marine environments such as petroleum pipelines. For many years a lot of research work has been carried out all over the world. In one study, it has been found that Al is very low resistant to the corrosive environment(3%NaCl) in static regime and corrosion processes onto the Al surface take place[1].

In another study, the effect of rain on Al alloy and galvanized steel roofing sheets was studied as well as their relative corrosion resistance [2]. The corrosion behavior of the pure Al after different immersion intervals in 3.5% NaCl solutions was also carried out and it indicates that the corrosion rate of Al is decreased with increasing immersion time due to the growing thickness of the corrosion product [3]. On the other hand, American Galvanizers Association (AGA) conducted tests of corrosion of galvanized steel in water collected from marine environments all over USA and it has been found that soft water, tropical sea water, high oxygen content causes higher corrosion in Zinc coating of galvanized steel [4]. In another study of copper the experimental determined that the weight loss of copper due to NaCl effect is significantly less than that of atmospheric condition by 0.002g[5]. In Bangladesh, roofing system in maximum houses of rural areas and few houses of urban areas involve using galvanized steel sheet. Usage of Cu and Al is very few as roofing sheet. Using of galvanized steel or substituting it with Al or Cu as roofing sheet or in plumbing applications is another field of interest in this research work. In this research paper, corrosion behavior of galvanized steel, Al and Cu has been investigated in three different types of aqueous environments.

2. Experimental Details

Galvanized steel sheet as well as the Al and Cu sheet of 4.5×2.0 cm size was taken as a main substrate and substitute substrate respectively. All the substrates were cut from the main sheet by hand shear cutting machine. The thickness of all substrates was 0.4mm. Area [A(decimeter^2)] of all the substrates was measured by slide calipars. All the substrates were cleaned with detergent, washed with acetone and dried. Initial weight [w_i(miligram)] of all the substrates were measured using electronic weighing balance machine. All the conditions were measured between 25^0C to 28^0C. After that all substrates were immersed in liquid environments (NaCl solution, Sea water and Rain water) respectively. For every liquid environment; five samples were dipped in five beakers containing the liquid and kept for 1,2,3,4 and 5 days (T) respectively. Then all the substrates were cleaned again with detergent, washed with acetone and dried. Finally, all the substrates final weight [w_f (miligram)] were measured. The weight loss is determined as difference between the initial and final losses after removal of the corrosion product by using electronic measuring device and hence calculation is used to measure the corrosion rate. CORROSION RATE= $\frac{Wi-Wf}{T*A}$; this formula is used to calculate corrosion rate. Corroded surface characteristics were observed using different types of test. XRD (X-ray diffractometer), XRF(x-ray fluorescence) test was undertaken. Finally, Scanning electron microscope (SEM) was employed to inspect the surface morphology of the base and corroded samples.

3. Results and Discussion

3.1Corrosive Environment: NaCl Solution

Galvanized steel exposed to NaCl solution shows decreasing corrosion rate with increasing exposed time. The value of corrosion rate or mdd for Al sample in NaCl environment is much lower than Galvanized steel. Al also shows decreasing corrosion rate with increasing exposed time [fig.1]. Chlorides are severely corrosive to zinc. So initially corrosion rate was high. As most of the zinc corrodes early; decreasing its concentration with time, decreases corrosion rate.

In the XRD pattern Zinc and chloride peaks were found [fig .2]. In XRF test , the amount of Zn (47.14%). So some Zn coating corrodes leaving behind residue in the beaker and also exposed Fe (32.25%) of the sample . Chlorides are severely corrosive to Al as its reactivity is high . So initially corrosion rate was high. As most of the Al corrodes early; decreasing its concentration with time, decreases corrosion rate. The XRD pattern [fig.3] of corroded sample shows only Al peak and a little disturbance or deviation from the standard one.

XRF indicates that Al (62%) whereas O (36.71%) and also some other impurities in minor amounts. O_2 and CO_2 come from distilled water [6] which forms protective film of aluminium oxide to resist further corrosion . Chlorides ions are very aggressive ions to copper and its alloys due to the tendency of the chloride ion to form an unstable film (CuCl)and soluble chloride complexes($CuCl_2^-$ and $CuCl_3^2$)[7].The formation of this CuCl film does not protect copper from dissolution in the chloride media. So initially corrosion rate was high. As most of the copper corrodes early; decreasing its concentration with time, decreases corrosion rate.

In Cu-O-H system, Cu and CuO_2 are the only stable solid phases if the fugacity of molecular hydrogen is maintained at a very low level. The XRD pattern shows[fig.5] the presence of Cu peak and CuO_2 peak. Maximum intensity for Cu occurs at ($2\theta=43^0$) and for CuO_2 it occurs at ($2\theta=36^0$).The ultimate reaction product on exposure of Cu to water is Copper hydroxide which is not well characterized using X-ray diffraction. Cupric ion (Cu^{2+}) is the most important state and is the oxidation state generally encountered in water and that’s why copper oxide peak has found. So the corrosion product in NaCl solution is copper oxide. The reaction is given below:-

$$Cu+OH^- \rightarrow Cu(OH)(ads)+e+$$
$$Cu+OH(ads) \rightarrow CuO_2+H_2O$$

XRF test indicates Cu(97.9194%) and Na(1.3692%),Cl(0.36345%).No free O found as it forms compound(CuO_2).

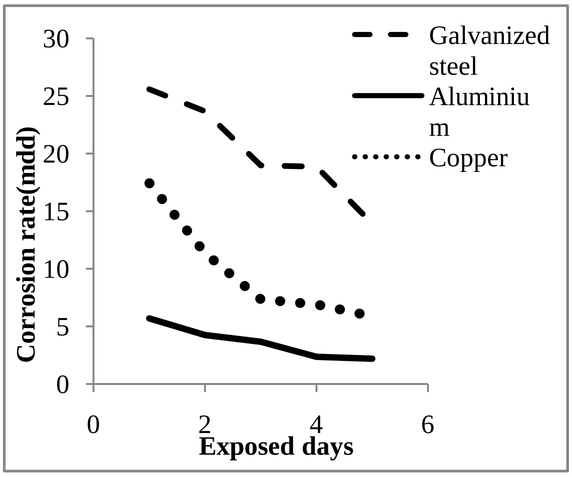

Figure 1. Corrosion rate vs exposed days

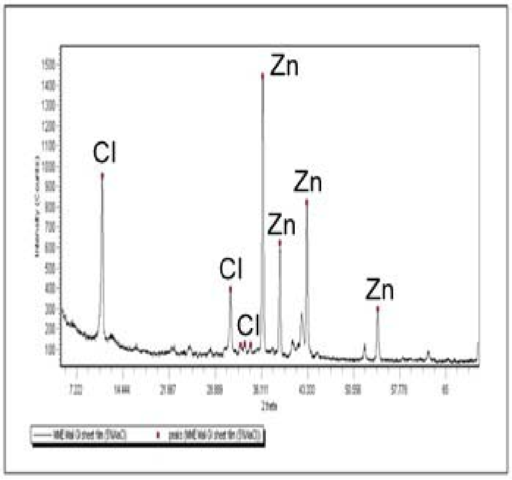

Figure 2.XRD analysis of Galvanized steel

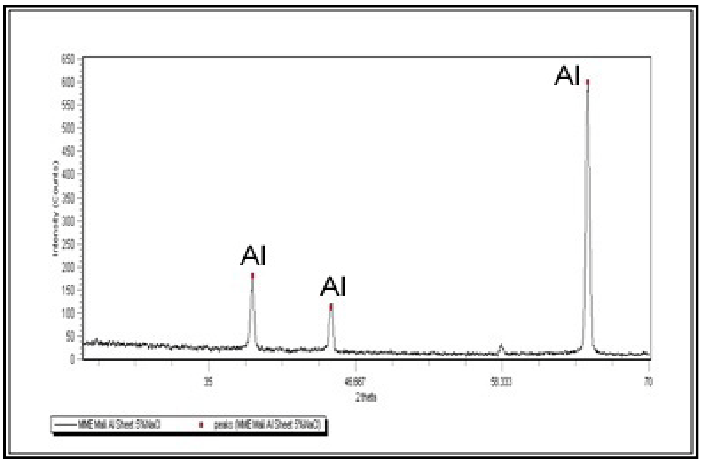

Figure 3.XRD analysis of Aluminium

3.2 Corrosive Environment: Sea Water

Sea water is high in salt content in the form of various chlorides and often sulfide is also detrimental [8]. It is a good electrolyte and corrosion is affected by oxygen content, temperature and biological organisms but it also contains carbonates. Carbonates form protective film on Zn surface . It also forms protective film on Al [8]. So corrosion rate in sea water is much lesser than NaCl solution in both samples[fig.4]. The presence of Ca and Mg ions also inhibits corrosion in the sea water because they form protective flim of carbonates .

XRD test of the galvanized steel sample ensures several peaks of Zn like in NaCl environment whereas XRD test of Al shows only Al peaks [fig.3]. XRF test of that sample ensures Zn (82.43%) so lesser amount of Zn corrodes than NaCl solution and exposed Fe (14.13%). For Al, XRF indicates Al (85.23%) and O (13.58%). Although corrosion curve in sea water shows increasing trend the value of mdd or corrosion rate is much lower. Corrosion of pure copper to sea water is believed to occur according to the following reaction:

Anodic reaction: $Cu \longrightarrow Cu^+ + e^-$

Cathodic reaction: $O_2+2H_2O+4e^- \longrightarrow 4OH^-$

Followed by the formation of cuprous complex,

$$Cu^+ + 2Cl^- \longrightarrow CuCl_2^-$$

Then cuprous oxide will be formed as:

$$CuCl_2^- + OH^- \longrightarrow CuO_2 + H_2O + Cl^-$$

According to the above equations the movement of O_2, OH^-,Cu^+ and $CuCl_2$ to and from the corroding surfaces will control the corrosion of Cu[10]. According to the mixed potential theory, increased transport of Cl^- or $CuCl_2$ to and from the surface will accelerate the anodic reaction, while the increase of O_2 transport will increase the cathodic reaction, so that corrosion rate will increase[fig.4] and vice versa.

The XRD pattern shows several number of CuO_2 peak [fig.5] whereas some Cu peak. Stable corrosion product(CuO_2) confirmed by XRD built up in the surface and reduce the mass transfer of O_2 and other agents to the metal surface resulting in the reduction of the kinetic of the cathodic reactions. Therefore, the increase in the corrosion product thickness decreases the corrosion rate.XRF test indicates Cu(99.3972%) and Cl(0.3970%) and no free O element as it forms stable CuO_2 compound.

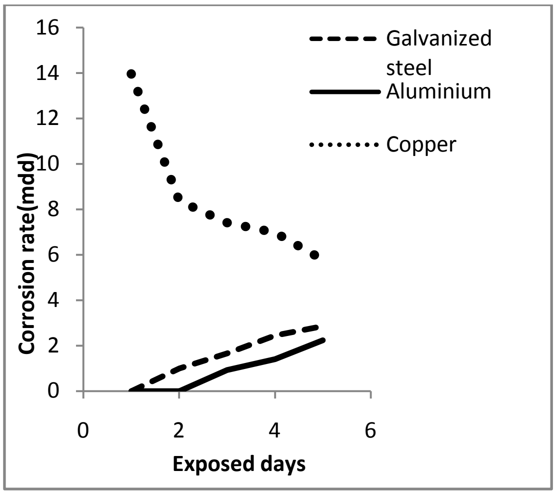

Figure 4. Corrosion rate vs exposed days

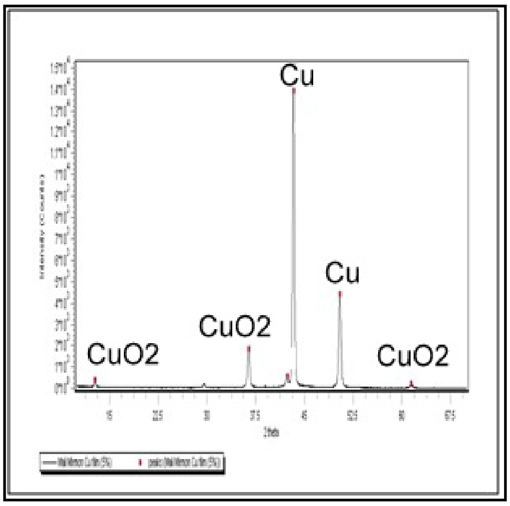

Figure 5.XRD analysis of Copper

3.3 Corrosive Environment: Rain Water

Rain water causes higher corrosion than that of the sea water. Rain water falls through atmosphere so it collects oxygen gas from atmosphere and dissolved in rain water which increases corrosion rate. The rain water is collected from Dhaka city. As the pollution is high in the Dhaka city, the rain is acidic in nature i.e. acid rain . So, corrosion rate is high. In the case of galvanized steel initially the amount of reactants is high but with increasing exposed day its amount decreases so inhibits corrosion rate[fig.6]. XRD test [fig. 7] ensures several peaks of Zn.

The XRD pattern shows more disturbance because of the formation of amorphous phase on the surface. The amorphous phase is Simonkollite [$Zn_5(OH)_8Cl_2.H_20$]. XRF test ensures Zn (77.01%) so more Zn corrodes than sea water and exposed Fe is (12.33%).In the case of Al corrosion rate increases [fig6] but the mdd values are very small. XRD shows only Al peak like that of NaCl solution and XRF indicates less aluminium deterioration (aluminium is 98.8% in corroded sample). Rain water causes higher corrosion. The XRD (Figure12.) pattern shows only Cu peak and no peak for stable compound CuO_2 .As a result with increasing time the rate of corrosion is increased. XRF test indicates Cu(99.6441%) and Cl (0.1127%) although the value of mdd is lower than that of sea water.

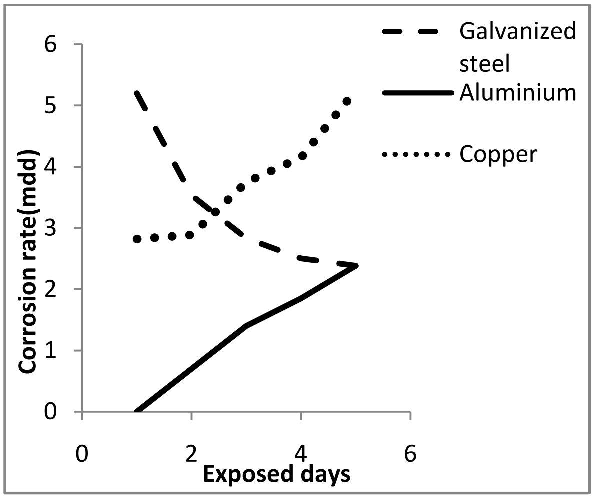

Figure 6. Corrosion rate vs exposed days

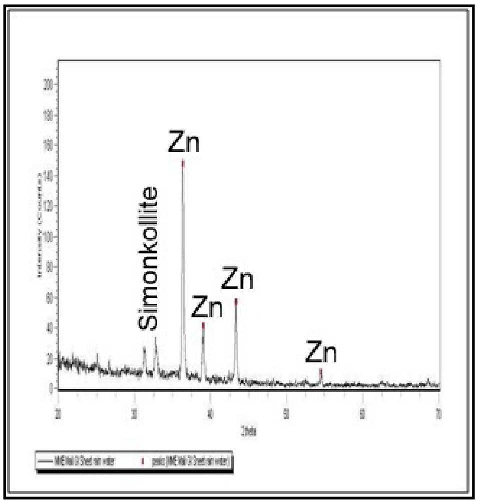

Figure 7. XRD analysis of galvanized steel

3.4 SEM Analysis for surface Morphology

SEM image of corroded galvanized steel sample is shown in figure 8. The sample was exposed five days in corrosive environment. The SEM image of sample immersed in NaCl solution shows some white corrosion product or nodules which are randomly arranged over the corroded surface to inhibit corrosion so corrosion rate decreased and also shows a separate layer on the surface. SEM image of corroded Al sample is shown in figure 9.These samples were also exposed five days in corrosive environments. This SEM shows corrosion product embedding on the surface which inhibits further corrosion of Al sample in these environment. Corrosion products wedging action causes the propagation of exfoliation attack [11] which increases the corrosion rate as time goes or number of days increased. The SEM image of the corroded copper sample is shown in figure 10. It shows numerous or several point defects or holes which are randomly distributed over the entire surface due to corrosion and some regions are not affected due to the formation of corrosion product (CuO_2).

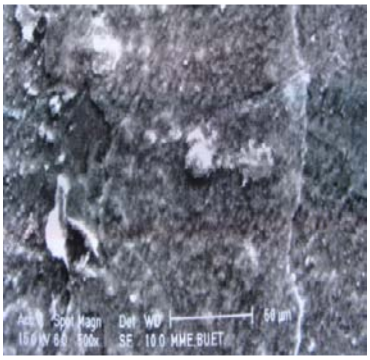

Figure 8.SEM of Galvanized Steel

Figure 9.SEM of Aluminium

Figure10.SEM of Copper

5. Conclusion

Corrosion test of Galvanized steel, aluminium and copper has been conducted. Compositional variation, corroded surface characteristics and surface morphology has been studied. Based on the experimental results and analysis, the following conclusions have been drawn:

1. The highest corrosion rate is found for galvanized steel (25.59) in NaCl environment whereas lowest value found in sea water (0).

2. Aluminium is the best material among the three considering all these aqueous environments.

3. Copper is better than galvanized steel only in NaCl solution and in rain water environments.

4. Corroded samples shows mainly small white nodules of corroded product ,corrosion products embedded on the surface and numerous point defects, holes randomly orientated for galvanized steel ,Al and Cu samples respectively.

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