# CORROSION OF GALVANIZED STEEL AND COPPER IN AQUEOUS ENVIRONMENTS

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***Abstract:*** *Corrosion test of galvanized steel and copper (Cu) has been carried out in three different aqueous environments e.g. 5% NaCl solution, sea water and rain water by immersion test technique. Corrosion rate is measured in mdd (mg/dm$^2$/day) unit. Corrosion characteristics of the corroded samples are investigated by XRD, XRF and SEM analysis. Irrespective of the exposure duration, Cu is seen better corrosion resistant than galvanized steel in 5% NaCl solution. Cu corrosion behavior is similar in 5% NaCl solution and the sea water as well. Formation of protective $Cu_2O$ scale on Cu surface is believed to decrease its corrosion rate with increasing exposure time both in 5% NaCl solution and sea water. Pitting corrosion occurs on Cu surface. For very short time exposure Cu is more corrosion resistant but galvanized steel becomes more useful than Cu for longer exposure in rain water.*

***Key words:*** *Corrosion rate (mdd), galvanized steel, copper, pitting corrosion, aqueous environment.*

## INTRODUCTION

Corrosion is a major problem for any engineering application. It increases production cost and properties of products are also worsen. Corrosion 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 threats to public safety, corrosion disrupts operations and requires extensive repair and replacement of failed assets. In Bangladesh, corrosion certainly is a considerable problem. So research on corrosion prevention is a vital need for better industrial production, public safety, health hazards etc.

Although metals are very important engineering materials, but the serious drawback to their mechanical and electrical properties is corrosion. Galvanized steel is used in aqueous environments in many indoor and outdoor applications where rust resistance is needed. It is also used in underground pipeline under sea water, frames to build houses and several household appliances. Galvanized steel involves zinc (Zn) coating on steel to prevent the underlying steel substrate from rusting. Zn is anodic to steel and thus it protects the steel by the mechanism called 'sacrificial protection'. American Galvanizers Association (AGA) conducted tests of corrosion of galvanized steel in water collected from marine environments all over the USA and it has been found that soft water, tropical sea water, high oxygen content cause higher corrosion in Zn coating of galvanized steel. In Bangladesh, roofing system in maximum houses of rural areas, specially in coastal areas and few houses of urban areas involve using galvanized steel sheet. On the other hand, copper (Cu) is one of the earliest metals intelligently used for practical applications when one considers the existence of human beings on this planet[1]. Cu is one of the most frequently encountered metals in our society. Cu and Cu-based alloys find applications in structural, architectural, marine and the electronics industry. Another important use of Cu is for canisters used in underground storage of high-level nuclear waste. The possibility of disposing of nuclear waste in Cu containers buried deep underground has been investigated[2]. Cu eventually forms a thin layer of corrosion, generally brownish-green or greenish-blue in color. This layer is called patina[3]. Once the patina is established it tends to be extremely stable and become a permanent part of the Cu object. Changes in patina, which can occur under some conditions, may be detrimental for the base metal. Cu corrosion products are known to have a protective effect against corrosion. However, a different behavior could be obtained in presence of pollutants (chlorides, sulfide etc.). This can be due to corrosion products morphology and degree of crystallization, rather than their phase composition[4].

Similarity in applications both for galvanized steel and Cu put them in similar environments like saline water, humid weather, rain water and so on. Corrosion is the major and common challenge of these two materials. Although a lot study has been conducted on the corrosion behavior of galvanized steel and Cu independently in various environments, corrosion tests of these two substrates in common environment is scarce. This work makes an attempt to study the corrosion behavior of galvanized steel and Cu in three aqueous environments e.g. 5% NaCl solution, sea water and rain water. Aqueous environments are chosen as corroding media because in real case scenario 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 sheet as well as the Cu sheet of 4.5×2.0 cm size was taken as the test sample. All the samples were cut from the main sheet by hand shear cutting machine. The thickness of both substrates was 0.5 mm. Area (A in $dm^2$) of all the substrates were measured by slide calipers. All the substrates were cleaned with detergent, washed with acetone and dried. Initial weight ($w_i$ mg) of all the substrates were measured using electronic weighing balance. The parameters were measured at ambient temperature. All substrates were then immersed in liquid environments (5%NaCl solution, sea water and rain water). 5% NaCl solution was prepared using deionized water and reagent grade NaCl salt, sea water was collected from the Bay of Bengal at Chittagong area, rain water was collected during raining in Dhaka city. For each environment, five samples were dipped in five beakers containing the liquid and kept there for T days (T = 1, 2, 3, 4 and 5 days respectively). Then all the substrates were cleaned again with detergent, washed with acetone and dried. Finally, weights ($w_f$ in mg) were measured for the substrates. Corrosion rate in mdd 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 = immersed time in day
A = Area of the sample in $dm^2$

Corroded surface characteristics were observed using XRD (X-ray diffractometer), XRF(X-ray fluorescence). Finally, Scanning electron microscope (SEM) was employed to inspect the surface morphology of the corroded samples.

## MECHANISM of Cu CORROSION in CHLORIDE SOLUTION

Bengough et al.[5,6] reported that mature, protective scales formed at the surface of Cu consist largely, but not entirely, of corrosion products. They assumed that in neutral chloride solutions, the main, initial corrosion product of Cu is cuprous chloride (CuCl) formed via reaction (1).

$$Cu^+ + Cl^- \rightarrow CuCl \qquad (1)$$

This film (CuCl) is unstable and it is supposed that CuCl reacts to produce cuprous oxide ($Cu_2O$) which is the main constituent of thick, protective scale[6]. The $Cu_2O$ generally oxidizes over time to cupric hydroxide ($Cu(OH)_2$). Later Lee and Noble[7] found that cuprous chloride complexes, $CuCl_3^{2-}$ and $CuCl_4^{3-}$ will be produced subsequently from $CuCl_2^-$ as shown by reaction (2).

$$Cu^+ + 2Cl^- \rightarrow CuCl_2^- + Cl^- \rightarrow CuCl_3^{2-} + Cl^- \rightarrow CuCl_4^{3-} \qquad (2)$$

The method of $Cu_2O$ production in the presence of the chloride ion is usually taken as a precipitation reaction[8,9] rather than a direct electrochemical or chemical formation from the base metal or cuprous chloride. The equilibrium in reaction (3) is shifted to the right as the local concentration of, for example, the $CuCl_2^-$ complex (produced directly from the dissolution of Cu metal or CuCl) increases and protective $Cu_2O$ is deposited.

$$2CuCl_2^- + 2OH^- \rightarrow Cu_2O + H_2O + 4Cl^- \qquad (3)$$

## RESULTS AND DISCUSSION

### Corrosion in Aqueous Environments

Change in corrosion rate with exposure time for galvanized steel and Cu in various environments is shown in Fig. 1. Scattered corrosion rate with exposure time both for galvanized steel and Cu is observed in various environments. For example, corrosion rate of galvanized steel decreases both in 5% NaCl solution and rain water but increases in sea water with increase of exposure time. On the other hand, decreasing trend of corrosion rate for Cu is observed both in 5% NaCl solution and sea water but it increases in rain water with exposure time. The corrosion behavior of galvanized steel and Cu in various environments is discussed separately in the following paragraphs.

### Corrosive environment: 5% NaCl solution

Both galvanized steel and Cu immersed in 5% NaCl solution shows decreasing corrosion rate with increasing exposure time [Fig. 1(a)]. The value of corrosion rate in mdd for Cu sample in NaCl environment is much lower than galvanized steel. Chlorides are severely corrosive to zinc. So initially corrosion rate was high. As most of the zinc corrodes early, decreasing chloride concentration in NaCl environment with time, corrosion rate decreases with increasing exposure time. Surface analyses of corroded samples by XRF test are shown in Table 1. Galvanized steel sample surface after corrosion in 5% NaCl solution contains 47.14% Zn, 32.25% Fe indicating major corrosion of the sample. Appearance of this corroded sample is shown in Fig. 2(a). The non-adherent corrosion products found in the beaker bottom are $ZnCl_2$ (white crystalline powder or granule). In the XRD pattern of corroded galvanized steel sample, Zn and chloride peaks are found [Fig. 3(a)].

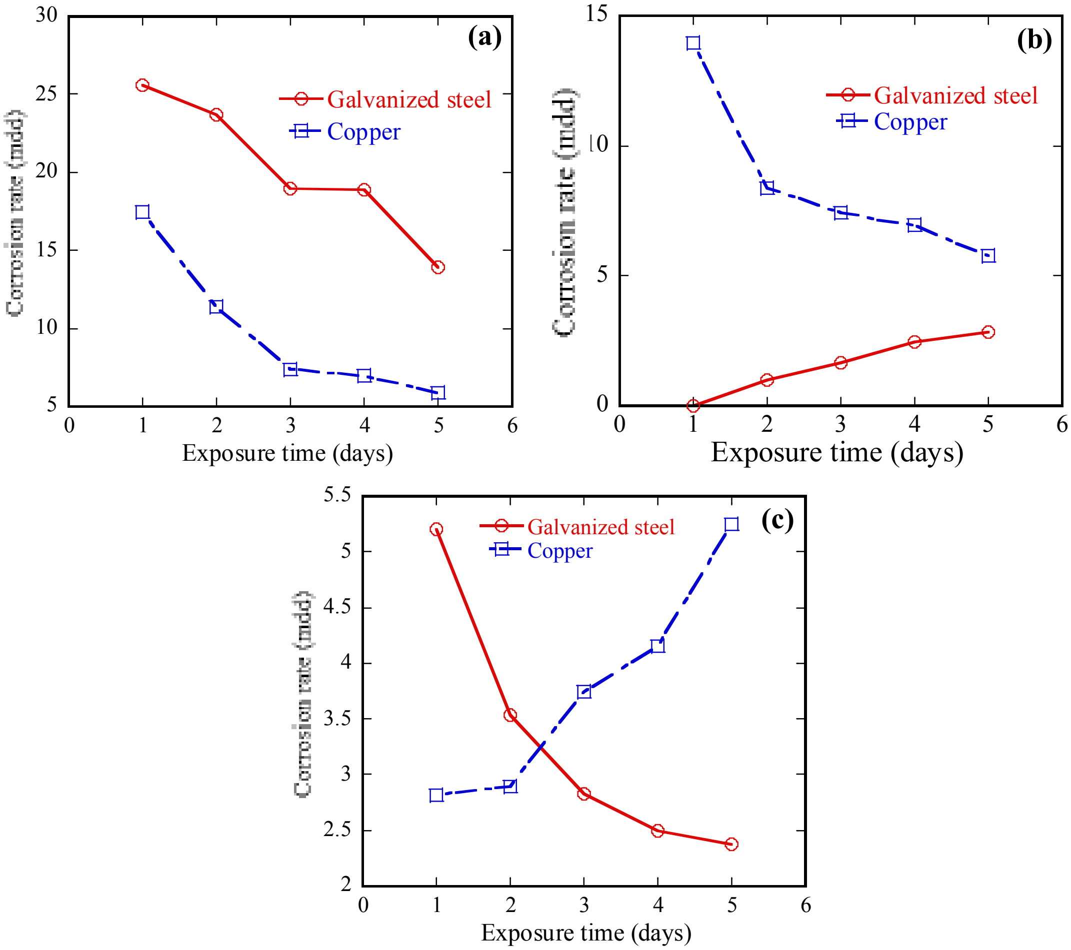

Figure 1. Corrosion rate as a function of exposure time of galvanized steel and Cu under immersion test in (a) 5% NaCl solution, (b) sea water and (c) rain water.

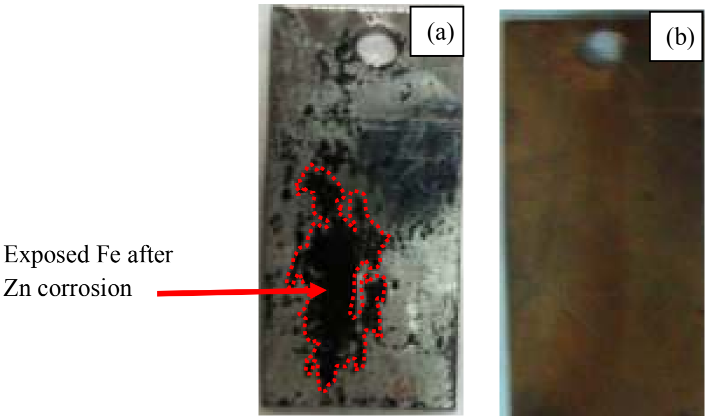

Figure 2. Corroded sample appearance of (a) galvanized steel and (b) Cu after 5 days immersion in 5% NaCl solution.

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 | |
| Cu | 5% NaCl solution | Cu | 97.92 | Moderate Cu corrosion |
| | | Cl | 0.36 | |
| | Sea water | Cu | 99.4 | Moderate Cu corrosion |
| | | Cl | 0.4 | |
| | Rain water | Cu | 99.64 | Less Cu corrosion |
| | | Cl | 0.11 | |

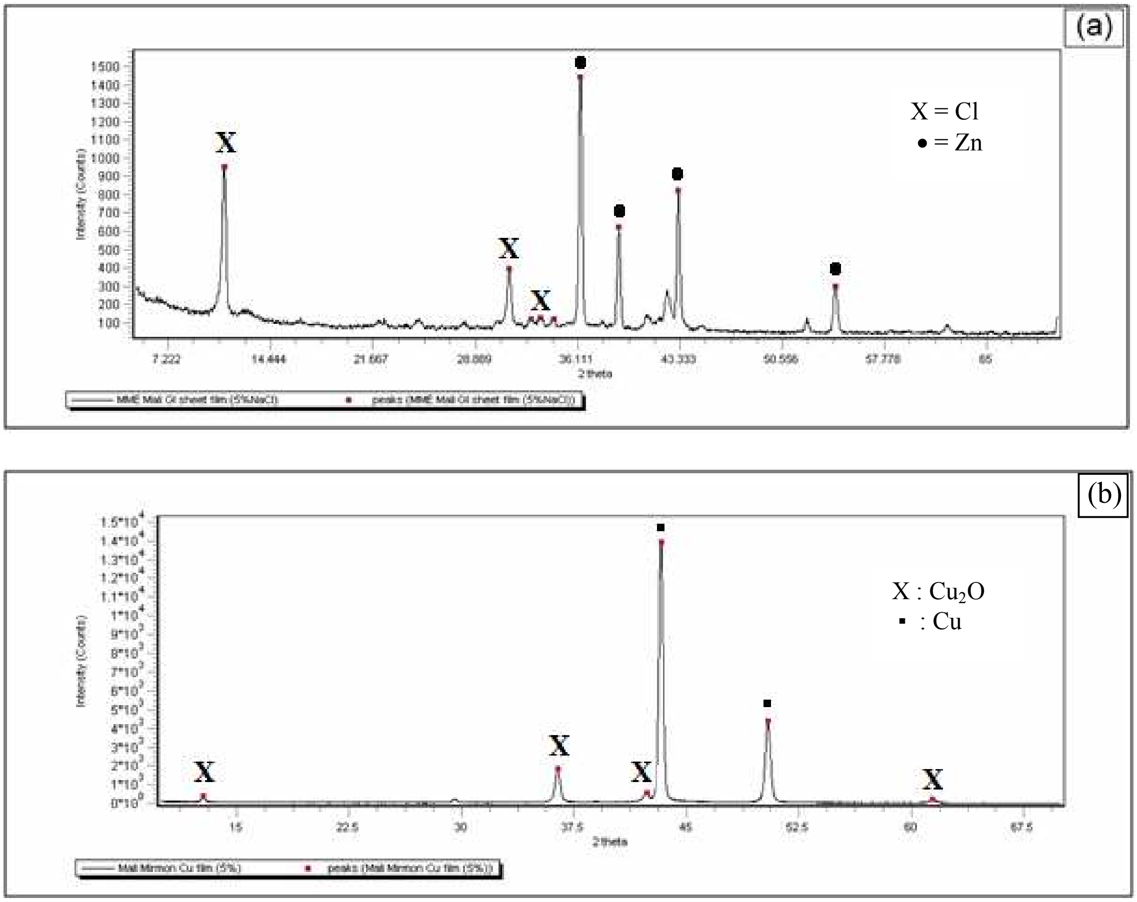

Figure 3. XRD pattern of (a) galvanized steel and (b) Cu after five days immersion in 5% NaCl solution.

Moderate Cu corrosion is supposed to be occurred in 5% NaCl solution revealing 97.92% Cu and 0.36% Cl as is seen in the XRF test. Following equation (1), the first corrosion product of Cu in chloride solution is unstable CuCl film and thus initially the corrosion rate is high. Subsequently CuCl reacts to produce cuprous oxide ($Cu_2O$) which is the main constituent of thick, protective scale[6] and thus corrosion rate decreases with increase in exposure time. Protective $Cu_2O$ might form in some other way as shown in equation (3) in response protecting further corrosion. Formation of protective $Cu_2O$ is supported by the XRD test result as shown in Fig. 3(b). Comparing the corrosion of galvanized steel with that of Cu in 5% NaCl solution, Cu is superior corrosion resistant than galvanized steel for short as well as long term basis.

**Corrosive environment: sea water**

Sea water is high in salt content in the form of various chlorides and often presence of sulfide in it is detrimental[10]. It is a good electrolyte and corrosion is affected by oxygen content, temperature and biological organism[11]. It also contains carbonates which form protective film on Zn (American Galvanizers Association) as well as on Cu surface[12]. So corrosion rate of galvanized steel in sea water is much lesser than in 5% NaCl solution. Corrosion rate gradually increases with increasing exposure time [Fig. 1(b)]. Although corrosion curve in sea water shows increasing trend, the absolute value in mdd is much lower than in 5% NaCl solution considering Y-axis scale. The presence of Ca and Mg ions also inhibits corrosion in the sea water because they form protective film of carbonates (American Galvanizers Association). Presence of 82.43% Zn in XRF test [Table 1] on the corroded galvanized steel sheet in sea water ensures the lesser amount of Zn surface corrosion than in 5% NaCl solution. This is further checked by only 14.13% Fe exposure of galvanized steel in sea water corrosion test.

For Cu sample, the corrosion behavior is almost similar to that observed in 5% NaCl solution. This is simply because the main constituent affecting Cu corrosion is chloride ion which is present in laboratory prepared 5% NaCl solution and the sea water as well. This will again be discussed in the subsequent corroded surface morphology section. XRF data [Table 1] indicates Cu and Cl contents are to be 99.4% and 0.4% respectively.

When the corrosion resistance of Cu is compared with that of galvanized steel in sea water, we see the decreasing corrosion rate of Cu and increasing corrosion rate of galvanized steel with the increase in exposure time. Although galvanized steel is seen better corrosion resistant than Cu within the test condition (5 days exposure time), Cu might be more corrosion resistant than galvanized steel for long time exposure. Further investigation considering longer exposure time is needed to confirm the result.

**Corrosive environment: rain water**

Rain water falls through atmosphere so it collects oxygen gas from atmosphere which increases corrosion rate. The rain water was collected from Dhaka city. As the pollution is high in the Dhaka city, the rain water is acidic in nature[13]. In the case of galvanized steel initially the amount of reactants is high but with increasing exposure time its amount decreases resulting inhibition of corrosion rate [Fig. 1(c)]. Thus initially corrosion rate of galvanized steel is high and it decreases with exposure time. XRF test [Table 1] ensures 77.01% Zn, so more Zn corrodes than sea water and exposed Fe is 12.33%. In the case of Cu, corrosion rate increases [Fig. 1(c)] but the mdd values are lower than that observed in other two environments. XRD test reveals only Cu peak. No protective $Cu_2O$ is developed in rain water corrosion. Thus corrosion rate increases with exposure time. XRF data of corroded Cu sample indicates 99.64% Cu and 0.11% Cl [Table 1]. Thus Cu corrosion becomes higher than galvanized steel in rain water for long time exposure (more than 2.5 days in this case).

**Surface Morphology of Corroded Sample**

SEM images of galvanized steel samples are shown in Fig. 4. The samples were exposed five days in corrosive environments. SEM image of the unetched base sample shows almost uniform surface [Fig. 4(a)] before corrosion test. Difference in surface elevation is 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. Sample corroded in sea water reveals few white nodules attached to the sample surface. Sample of rain water shows some corrosion products or nodules [Fig. 4(d)]. These are small in number randomly oriented over the surface.

SEM images of Cu samples are shown in Fig. 5. These samples were also exposed five days in corrosive environment. SEM image of the unetched base sample shows almost uniform surface [Fig. 5(a)]. Difference in surface elevation is visible as the sample surface is not polished. Pitting corrosion appearance is observed both on the SEM images of the Cu sample corroded in 5% NaCl solution and sea water [Fig. 5(b) and (c)]. Main constituent in 5% NaCl solution and sea water is chloride ion which is the major corroding ingredients for Cu. Similar corrosion rate with exposure time is also observed in Fig. 1(a) and (b). Minor difference in the corrosion extent is visible in Fig. 1 which is reflected in Fig. 5. Corrosion of Cu after 5 days exposure is the minimum in rain water. A few corrosion marks (not pitting) is visible on the microstructure of Cu corroded sample in rain water.

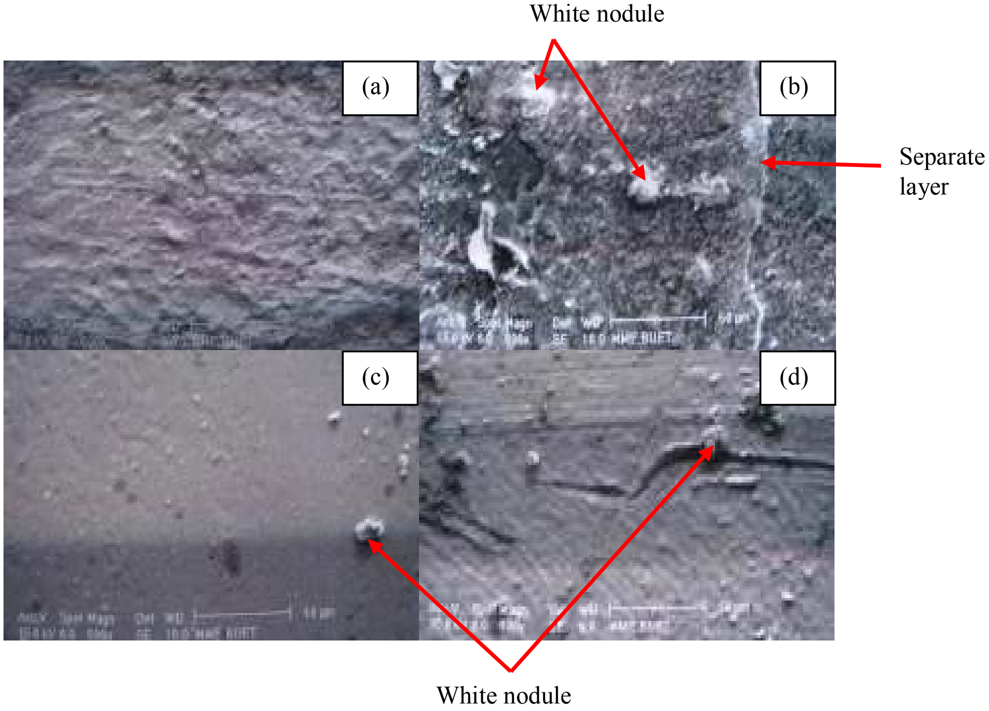

Figure 4. SEM of galvanized steel (a) before corrosion; after corrosion in (b) 5% NaCl solution; (c) sea water and (d) rain water. All corrosion tests were continued for 5 days.

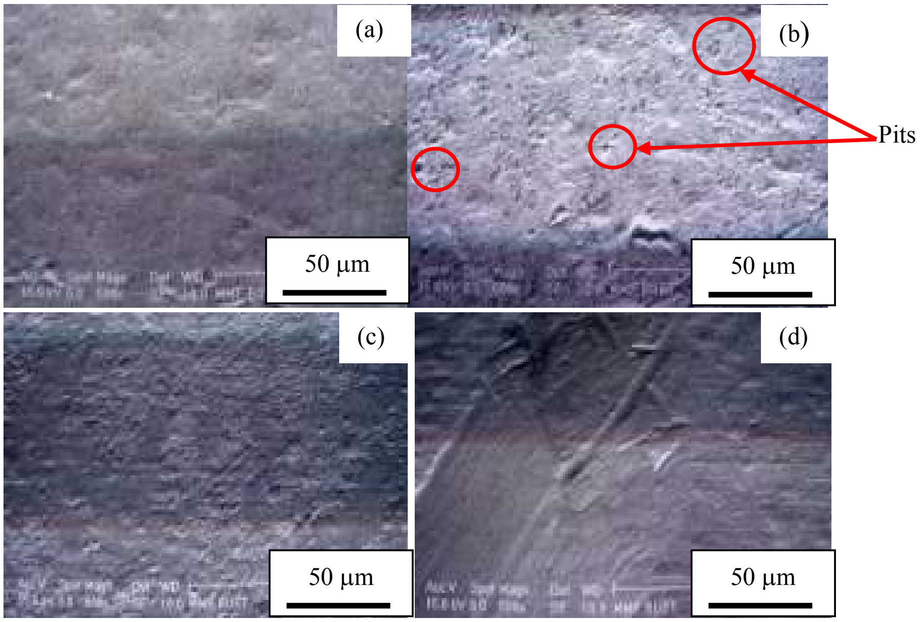

Figure 5. SEM of Cu sheet (a) before corrosion; after corrosion in (b) 5% NaCl solution; (c) sea water and (d) rain water. All corrosion tests were continued for 5 days.

## CONCLUSION

Corrosion test of galvanized steel and Cu 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:

- Cu is superior corrosion resistant than galvanized steel in 5% NaCl solution irrespective of the exposure duration.

- Galvanized steel is better corrosion resistant than Cu up to 5 days exposure in sea water. Decreasing corrosion trend of Cu and increasing corrosion trend of galvanized steel indicates that Cu might be more corrosion resistant than galvanized steel for too long exposure time.

- For very short time exposure Cu is more corrosion resistant but galvanized steel is more useful than Cu for long time exposure in rain water.

- Initially unstable CuCl forms on Cu surface upon exposure in chloride environment. With the progress of time, CuCl transfers to $Cu_2O$ which is stable and protective. Thus corrosion of Cu in 5% NaCl solution as well as sea water decreases with increase in exposure time.

## REFERENCES

1. Balasubramaniam, R., “Archaeo-metallurgy of Ancient Indian Copper”, Trans Indian Inst Met., in Press.
2. Werme, L. O. and Sellin, P., 2003, “The Performance of Copper Canister for Geologic Disposal of Spent Nuclear Fuel in Granitic Rock”, Proc., International Workshop on Prediction of Long Term Corrosion Behavior in Nuclear Waste Systems, European Federation of Corrosion, D. Feron et al., eds., The Institute of Materials, Minerals and Mining, London 7, 36, pp. 395– 411.
3. Graedel, T. E., Nassau, K. and Franey, J. P., 1987, “Copper Patinas Formed in the Atmosphere”, Corros Sci., 27, pp. 639–657.
4. Mendoza, A. R., Corvo, F., Go´mez, A. and Go´mez, J., 2004, “Influence of the Corrosion Products of Copper on its Atmospheric Corrosion Kinetics in Tropical Climate”, Corros Sci., 46, pp. 1189– 1200.
5. Bengough, G. D., Jones, R. M. and Pirret, R., 1920, “Diagnosis of Brass Condenser Tube Corrosion”, J. of the Institute of Metals, 23, pp. 65–158.
6. Bengough, G. D. and May, R., 1924, J. of the Institute of Metals, 32, pp. 81–269.
7. Lee, H. P. and Nobe, K.,1986, “Kinetics and Mechanisms of Cu Electrodissolution in Chloride Media”, J. of the Electrochemical Society, 133**,** pp. 2035–2043.
8. Bianchi, G., Fiori, G., Longhi, P. and Mazza, F., 1978, “Horse Shoe Corrosion of Copper Alloys in Protection of Condenser Tubes in Power Stations”, Corrosion-NACE, 34, pp. 396–406.
9. Faita, G., Fiori, G. and Salvadore, D., 1975, “Copper Behaviour in Acid and Alkaline Brines”, Corrosion Science, 15, pp. 383–392.
10. Jayaraman, R., 1951, “Observations on the Chemistry of the Waters of the Bay of Bengal of Madras City During 1948 – 1949”, Proc. of the Indian Academy of Sciences, 33b (2), pp. 92-100.
11. Al-Fozan, S. A. and Malik, A. U., 2005, “Effect of Seawater Level on Corrosion Behavior of Different Alloys”, Int. Desalination Association (IDA) World Congress Conference, Singapore, pp. 1-11.
12. Wan Nik, W. B., Sulaiman, O., Fadhli, A. and Rosliza, R., 2010, “Corrosion Behavior of Aluminum Alloy in Seawater”, Proc., Int. Conference on Marine Technology, MARTEC 2010, pp. 175-180.
13. Abdulkarim, B. I., Abdullahi, Y. A. and Salam, K. A., 2009, “Corrosion Resistance of Commercial Roofing Sheets to Acid Rain Water in Eleme, Rivers, Nigeria”, Int. J. of Chem. Tech. Research, 1(4), pp. 802-806.