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## Corrosion Behavior of Work Hardened Commercial Copper Alloys in the Bay of Bengal Water Environment

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### ABSTRACT

Corrosion behaviors of metals and alloys have been studied by different researchers for different oceans and seas to have comprehensive design variables for optimum operations and maintenance of ships, offshore structures and marine machineries as well as systems. Unfortunately, the Bay of Bengal has not become very efficacious to draw required attention in relation to corrosion study especially for those metallic materials which are generally considered as corrosion resistant. Therefore, present paper is an attempt to investigate the corrosion behavior of three copper based materials, i.e., pure copper, brass and bronze which are being used in contact of the bay water. Here, the results of gravimetric analysis, conductivity tests, optical electronic microscope (OEM) images, scanning electron microscopy (SEM) images and energy dispersive X-ray analyzer (EDX) investigations have been presented. Gravimetric analysis has established that the total corrosion of all copper based materials have been increased gradually but nonlinearly with the increase of exposure periods in sea water. After the immersion period of 27 days, pure copper is found to be the most corrosion resistant amongst three sample materials and brass is the least one, where bronze is found to be in between the rest two. The corrosion rate profiles have shown an initial steep rise, but with the increase of submersion period the rates are reduced with subsequent steady values for prolong exposure in sea water. Microstructures observed through OEM and SEM images have clearly indicated a general uniform surface corrosion with little crystallographic pitting spots after exposure in sea water.

**Keywords:** Copper Alloys, Sea Water, Gravimetric Analysis, Corrosion Rate

### 1. Introduction

Endeavors to exploit the ocean and sea have been the long term activity of human civilization, which have gained considerable momentum in recent years due to increased utilization of seawater as a medium of transportation, energy generation, oil and mineral exploration and many other purposes [1]. The very sea based activities have a direct impact on problems associated with the maintenance of marine vehicles, structures and machineries due to aggressive effect of sea water on them. Thus the considerations of merit before a material is recommended for ocean services are the structural strength, predicted life expectancy, acquaintance of uncertainty and most importantly the corrosion behavior. Basically, marine corrosion is an economically important problem facing all the maritime nations of the world [2].

In this context, copper and its alloys including brass or bronze are very popular to mariners and widely used by shipbuilders to good effect in the marine applications for high corrosion resistance along with required mechanical properties. However, copper based materials are not totally immune from corrosion effect especially in contact of sea water [3, 4]. The factors which affect the amount of material loss and rate of corrosion in sea

water are of physical, mechanical, chemical or biological due to oxygen content, relative velocity, temperature variation, micro-biological activities, salinity level and pH value of seawater [5]. Moreover, alloying elements and work hardening have bearings on the corrosion behavior of copper based materials [4, 6]. Many types of corrosion attack can occur to the marine structure, ship and equipment that made up of copper based alloys exposed to sea water. Distinctive attacks on copper based alloys may include impingement attack, dezincification, denickelification, fretting, pitting, crevice etc. [5, 7-9]. High chloride content of seawater and dissolved gases usually play the vital roles in corrosion attacks, especially to increase the rate of dezincification and forfeiture of surface particles [10-12]. While the relative water speed is low and the deposits can settle on the surface, pitting on copper and copper alloys is liable to occur [13, 14]. Moreover, the sea water contents especially the salinity, dissolved oxygen, total suspended solids (TSS), total dissolved solids (TDS), sulfate, chloride etc. may vary from ocean to ocean, which cause the variation of corrosion behaviour of copper alloys [5, 8-9].

Several research works can be cited which have been carried out over the world for different seas and gulfs such as sea water of Peruvian Port [8], seawater

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systems on Norwegian Continental Shelf [9], seawater of tropical island [15], Seawater of Gulf of Mexico [16], water of North Atlantic Ocean [17] and many more. All these literatures are having distinct findings and observations for their own. But the Bay of Bengal has remained aloof from adequate attention to carry out corrosion study. Since a good number of sea borne activities are going on in this bay, it is very important to carry out the study of corrosion behavior of copper based alloys being used in the water of the Bay of Bengal as propeller, shaft fittings, bushes, etc. Therefore, this paper takes an effort to characterize the corrosion rate of brass and bronze in comparison to pure copper coming in contact of sea water. In this study, gravimetric analysis of corrosion is investigated along with the variation of conductivity and microstructure due to such corrosion.

## 2. Materials and Methods

### 2.1 Sample Preparation

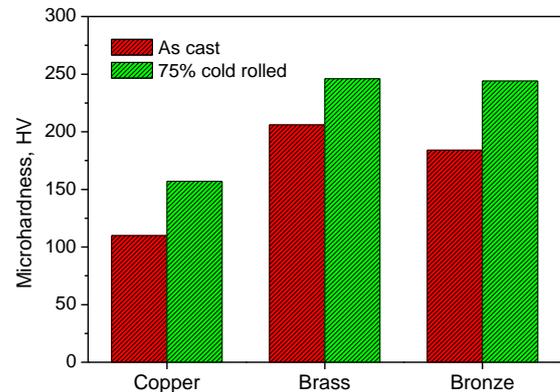
Since brass and bronze are the most promising copper based alloys used in the vessels as well as systems by the mariners, these two alloys were collected from the local market of Bangladesh to carry out the present study. The said alloy materials were taken in conjunction to the copper ingots for comparison purpose. The chemical compositions of these three types of sample materials were examined using X-Ray Fluorescence (XRF) spectrometer of model Olympus DPO-2000-CC and the values obtained are presented in table 1.

**Table 1** Chemical composition of samples (mass fraction %).

Elements	Cu	Sn	Zn	Pb	Fe	Ni	Si	P
Copper	99.63	-	-	-	-	-	0.14	0.23
Brass	60.77	-	37.28	1.58	0.22	0.15	-	-
Bronze	95.21	4.32	-	0.10	-	-	-	0.37

From each type of materials, flat bars of size 300 x 15 x 12 mm were made through cutting and machining precisely so that surface grains remained least affected. These flat bars were at first homogenized for eight hours at a temperature of 500°C for the reduction of chemical segregation and then solution treated for two hours at a temperature of 700°C to improve their workability. Then work hardening was done using roller machine operated at room temperature such that the thickness of the flat bars could be reduced from 12 mm to 3 mm (75% cold rolled work hardened). Here, minimum feed was applied for roll pass, and thus, the number of roll passes was the maximum to avoid thermal effect during rolling operations. To comprehend the actual work hardening effect on the sample materials, micro-hardness values before and after the cold rolling, i.e., as cast and as 75% rolled were investigated using Vickers Hardness Tester (HV-100)

with 1 kgf load applied for 10 seconds. The variation in this regard is presented in figure 1.



**Fig.1** The variation of micro-hardness for the experimental sample alloys.

It is observed that alloying of copper has increased the micro-hardness significantly for both the alloys such as brass and bronze. As cast condition, the micro-hardness values of brass and bronze are 1.886 and 1.662 times higher, respectively, than that of copper. After cold rolling of 75% deformation, micro-hardness values of all three sample materials i.e., copper, brass and bronze have been increased by 44.6%, 19.1% and 34.4% with respect to their as cast values.

Then all the three work hardened materials were sized up of 56 mm x 15 mm x 3 mm to carry out the examinations. The sized up coupons were then mechanically ground with 160, 300, 600, 900 and 1200 grits of SiC emery paper successively. On completion of dry polishing, all the samples were wet polished using alumina paste and dried up at room temperature in natural ventilation.

**Table 2** Contents/properties of sea water used for the investigation of corrosion

Parameter	Values
pH	7.14
Total Dissolved Solids (mg/liter)	28000
Total Suspended Solids (mg/liter)	48
Chloride (mg/liter)	21000
Sulphate (mg/liter)	1320
Dissolved Oxygen (mg/liter)	7.29
Electric Conductivity ( $\mu$ S/cm)	48000

### 2.2 Experimental Details

To investigate the corrosion behavior of copper and its two popular alloys namely brass and bronze, sea water (about 800 liter) was collected from the Bay of Bengal (about 15 nm down from the coastline). Its ingredients and main properties were examined using different testing devices such as pH meter for pH value,

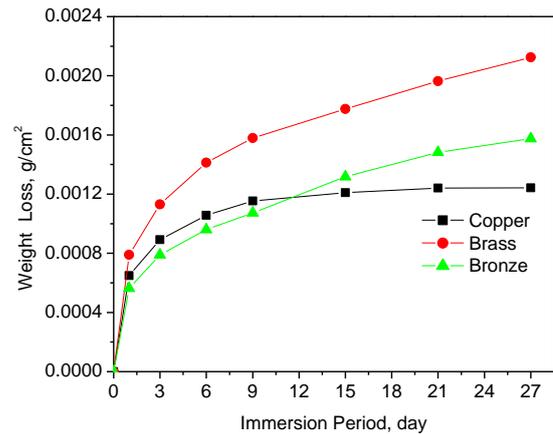
turbidity meter for TSS, conductivity meter for TDS and electric conductivity, titrimetric analysis for sulfate and Chloride, and DO meter for dissolved oxygen. The obtained results of sea water ingredient/property tests are shown in table 2. The sea water was then placed in 12 beakers having being covered to avoid evaporation and protection from dust inclusion at the room temperature for immersion of sample coupons.

The prepared samples were at first examined for the microstructure using computer interfaced Optical Electronic Microscope (OEM) of model BW-S500. Thereafter, the electrical conductivity values of the samples were measured using digital Type 979 Meter with an accuracy of  $\pm 0.1\%$  IACS (International Annealed Copper Standard) and the samples were weighed as well as dimensions were measured before their immersion in the sea water beakers. The weighing machine of model Sartorius Entris 224-1S having 0.1mg precision and ultrasonic thickness gauge of model CG100 ABDL were used for the experimental purposes. Then the sample coupons were submerged in the stagnant sea water placed in beakers. Precautions were taken so that coupons could remain fully immersed as well as untouched from wall of beaker so that all the surfaces of the sample are in contact of sea water. On completion of 24 hours immersion in sea water, coupons were removed for a while to examine weight, dimensions, conductivity and microstructure. After taking all the readings very quickly, the coupons were placed again in the beakers. Similar readings were taken after 3 days, 6 days, 9 days, 15 days, 21 days and 27 days immersion of samples in the stagnant water of Bay of Bengal, successively.

### 3. Results and Discussions

#### 3.1 Gravimetric Analysis

Sea water is well known as a severe corrosion agent because it is a complex electrolyte solution of relatively high concentration of many salts, living matters, suspended silts and dissolved gases. It has also been observed in the water of Bay of Bengal as indicated in table 2. As such, having been status of noble metal family member, copper materials could not remain immune from corrosion in the aggressive sea water environment, and thus, they have demonstrated the loss of weight per exposed surface area against immersion period. Figure 2 depicts that all three sample materials have shown almost similar weight loss trends against immersion period. Initially, all three curves are found to be steeper indicating higher amount of weight loss per exposed surface area due to the first attack of sea water ingredients. Thereafter, weight loss tendencies of all three sample materials have been reduced with the increase of immersion period. The high reduction in weight at the initial period of submersion might be the consequence of time required for gradual formation of patina on the exposed surface [18-19].



**Fig. 2** Variation of weight loss per exposed surface area ( $\text{g}/\text{cm}^2$ ) as a function of immersion period (days) in sea water for copper, brass and bronze.

Moreover, Fig. 2 indicates that the weight reduction rates have been found to be different for three sample materials. During initial days of the experiments, bronze has shown the lowest weight loss behavior with the indication of highest corrosion resistance (green line in Fig. 2) and brass shows the highest (red line in Fig. 2), where pure copper remains in between them (black line in Fig. 2). But the weight loss curve of bronze overshoots the curve of copper in between the immersion periods of 9 days and 15 days in sea water, approximately at 12 days. The results at 15 days onwards depict that copper is losing the lowest weight amongst three sample materials, where brass continues to be the highest and bronze in between. The weight loss curve of copper has become almost horizontal showing zero gradient of weight reduction after the immersion period of 27 days. But brass and bronze have continued to lose their weight with the increase of immersion period. Once patina is formed, corrosion of pure copper is reduced. However, the continuation in weight loss for brass and bronze with the increase of immersion period has occurred due to the differential corrosion effect of constituents of these two materials.

The cumulative values of weight losses per exposed surface area for copper, brass and bronze after the immersion period of 27 days in sea water are found to be  $1.24 \text{ mg}/\text{cm}^2$ ,  $2.12 \text{ mg}/\text{cm}^2$  and  $1.57 \text{ mg}/\text{cm}^2$ , respectively. As a result, the total reductions from their original values of weight are 0.25%, 0.41% and 0.32%, respectively.

The corrosion rates of all three sample materials have been calculated based on weight loss data using following expression [20]:

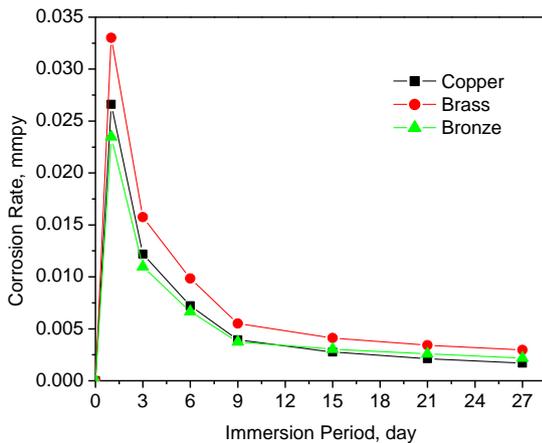
$$R_{\text{Corr}} = \frac{(K \times \Delta W)}{(\rho \times T)}$$

Where,

$R_{\text{Corr}}$  = Corrosion Rate (mm/year)

$\Delta W$  = Weight loss per exposed surface area ( $\text{gm}/\text{cm}^2$ )  
 $K$  = Unit conversion factor  
 $\rho$  = Density of metal ( $\text{gm}/\text{cm}^3$ )  
 $T$  = Exposed time (hour)

Figure 3 depicts that the corrosion rates of all three sample materials, i.e., copper, brass and bronze have been found to be the highest for the immersion period of the first 24 hours with the values of 0.026 mmpy, 0.033 mmpy and 0.023 mmpy, respectively. Thereafter, with the increase of exposure period, all three sample materials have shown gradual falling trends of corrosion rates and finally after 27 days of observation, the values are found to be only 0.0017 mmpy, 0.0029 mmpy and 0.0022 mmpy, respectively. Figure 3 also indicates that the corrosion rate curve of brass remains on the top all over the immersion period. The corrosion rate curve of pure copper has followed the curve of brass. The corrosion rate of bronze is the lowest at the initial immersion period as seen for weight loss and it crossed the value of pure copper after the immersion period of about 12 days. However, both the corrosion rate curves (for copper and bronze) are found to be very close to each other.

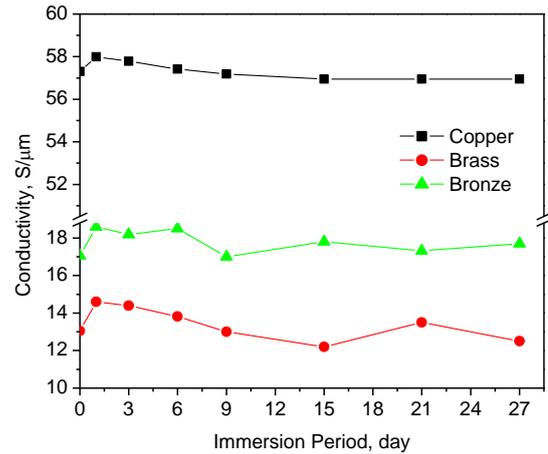


**Fig. 3** Variation of corrosion rate (mm per year) as a function of immersion period (days) in sea water for copper, brass and bronze.

### 3.2 Conductivity Investigation

The conductivity values of all three work hardened sample materials have not been severely affected after their immersion in the aggressive environment of sea water. Figure 4 indicates that the conductivity of pure copper has varied a bit just after immersion and then has remained almost the same over the exposed period of 27 days in the sea water. The steady values of conductivity indicate that the dissolution has occurred uniformly over the pure copper surface. At the first attack conductivity values of brass and bronze have also increased like pure copper, but there are fluctuations in conductivity values with respect to immersion period. The ranges of such

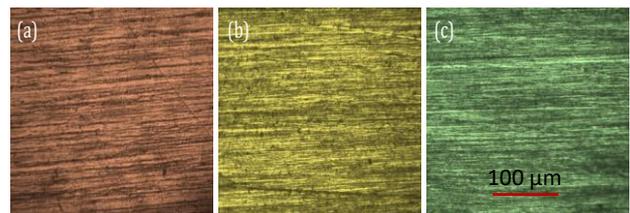
fluctuations (minimum to maximum values) are  $12.2 \times 10^6 \text{ Sm}^{-1}$  to  $14.6 \times 10^6 \text{ Sm}^{-1}$  for brass and  $17.1 \times 10^6 \text{ Sm}^{-1}$  to  $18.6 \times 10^6 \text{ Sm}^{-1}$  for bronze, which give the standard deviations of  $0.803 \times 10^6 \text{ Sm}^{-1}$  and  $0.583 \times 10^6 \text{ Sm}^{-1}$ , respectively. These fluctuations of conductivity for brass and bronze are considered to be the result of pit formation and diffusion of aggressive ions in contact of sea water leading to porosity on the surface at irregular forms due to presence of alloying elements with varied polar values. However, no direct relation could have been observed between the conductivity and the corrosion rate of copper based materials.



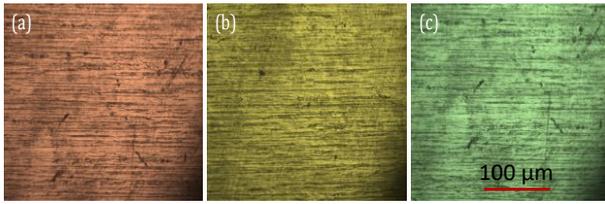
**Fig. 4** The variation of conductivity as a function of immersion period in sea water for copper, brass and bronze.

### 3.3 Microstructural Investigation

Micrographs observed using OEM before corrosion test and after 27 days immersion in the sea water are presented in figures 5 and 6 respectively. The OEM images in figure 5 indicate smooth surfaces of the work hardened sample materials with natural polishing marks. But after 30 days immersions in the environment of sea water, the microstructures of samples have been observed with distinct signs of corrosion (figure 6). The polishing marks have been faded away from the sample surfaces due to global corrosion effect which eventually gives the indication of the weight loss and corrosion rate during gravimetric observation shown in figures 2 and 3.

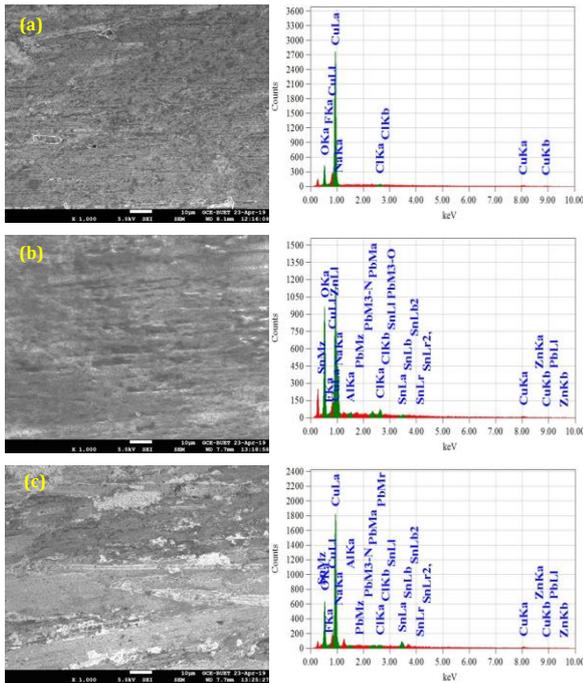


**Fig. 5** OEM images of sample materials with magnification factor of 180 before immersion in sea water: (a) Copper, (b) Brass and (c) Bronze.



**Fig. 6** OEM images of three material samples with magnification factor of 180 after 27 days immersion in sea water: (a) Copper, (b) Brass and (c) Bronze.

FE-SEM images with EDX spectra are presented in Figures 7(a), 7(b) and 7(c) for three sample materials respectively. These figures indicate some noticeable corrosion products and few pits with randomly nucleated orientations of crystals. It is considered that the pits have been formed either by intermetallic dropping out from the surface due to the dissolution of the surrounding matrix or selective dissolutions of the intermetallic or particle during immersion period. Brass is corroded more than other two sample materials due to dezincification.



**Fig. 7** SEM images with EDX spectra of three material samples with magnification factor of 1000x after 27 days immersion: (a) Copper, (b) Brass and (c) Bronze.

The mass percentage of elements found by EDX profile analysis of the SEM for corroded copper are found as 12.22% O, 0.46% Cl, and 87.32% Cu. The mass percentage of elements found by EDX profile analysis of the SEM for corroded brass are found as 38.09% O, 2.37% Na, 0.16% Al, 2.49% Cl, 35.59% Cu, 17.54% Zn, and 3.75% Pb. The mass percentage of elements found by EDX profile analysis of the SEM for

corroded bronze are found as 23.72% O, 0.10% Al, 0.19% Cl, 62.43% Cu, 12.88% Sn and 0.68% Pb. It indicates that the sea water corrosion has the effect on the chemical composition of the surface constituents of the material which results in significant percentage of oxygen along with some amount of chlorine. It has happened due to oxidation effect and presence of diversified elements and compounds in sea water in forms of salt, micro-organisms, minerals etc.

#### 4. CONCLUSIONS

The sea water is a complex chemical system affected by several factors such as pH, salinity, dissolved gases, conductivity and many others. Moreover, the sea water contents may vary from ocean to ocean which results in the variation of corrosion behavior of copper alloys. The present investigation carried out in the water of the Bay of Bengal indicates that none amongst the three sample materials (copper, brass and bronze) is immune from corrosion after work hardening. Amongst them brass is found to be the most corrosive. Bronze is the corrosion resistant for short period of immersion but copper is most corrosion resistant while immersion is prolonged.

The conductivity has not been significantly affected over the period in contact of the bay water. However, there are little fluctuations in conductivity values due to corroded surface and small pit formations. The microstructures observed through OEM and SEM images of the corroded surfaces have also confirmed the non-immunity of copper based materials. Another issue is the change of chemical composition on the surface particulates after corrosion effect. Therefore, corrosion behavior of copper alloys need to be taken into account for the reliability in marine applications.

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