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## Corrosion and microfouling of copper and its alloys in a tropical marine waters of India (Mangalore)

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Rate of corrosion, extent and nature of microfouling of copper, cupronickel 70/30 and cupronickel 90/10 have been studied for three different seasons at a station on the west coast of India. The corrosion rates for all the three materials are higher during premonsoon as compared to other two seasons. Decreasing trend in the corrosion rate has been observed with increased nickel content. The microfouling assemblage which is estimated in terms of diatoms and bacterial count and their exopolysaccharide exhibited inverse relationship with corrosion rate. Marked seasonal variations in the extent of corrosion and microfouling are evident. The resistivity of copper and its alloys towards microfouling has been found to be in the order as  $\text{Cu} > \text{Cu-Ni 90/10} > \text{Cu-Ni 70/30}$ . X-ray diffraction analysis of the corrosion products revealed the presence of  $\text{Cu}_2\text{O}$  as major component in both the alloys.

Recently, copper and its alloys have achieved great importance in marine applications due to their resistivity to marine corrosion and biofouling. These materials are used in ship's piping systems, ship's hulls, fish cages, condensers, intake screens and offshore platforms<sup>1,2</sup>. The antifouling efficiency of copper and its alloys is dependent on the rate at which they react with the marine waters. It has been reported that more than  $10 \mu\text{g}/\text{cm}^2/\text{day}$  leaching of copper would prevent macrofoulers. However, despite the toxic nature, these materials have been found to be fouled by some members of microfouling community<sup>3</sup>. This is mainly because of the development of resistance due to secretion of sheath or extracellular polysaccharides (EPS) by the microfoulers. The extracellular polysaccharides of microfoulers operate as detoxification mechanism by means of encapsulation of cells or binding of large quantities of toxic ions<sup>4-6</sup>. The EPS produced by some of the microfoulers especially bacteria and diatoms may affect corrosion rate of metals in marine environment<sup>7,8</sup>. It has been observed<sup>9</sup> that the extent of EPS production in a fouling diatom species depends on the nutritional status of the environment.

Corrosion and biofouling are considered as site specific processes and are mainly dependent on the extent of physical, chemical and biological factors. These factors are the characteristic of the environment at a given site. Both these processes are known to influence each other directly or indirectly<sup>9</sup>. It is a well known fact that the severity of both these

processes is more in tropical than in temperate waters<sup>9</sup>. That is why the tropical environment is being studied widely for biofouling aspects. However, the information relating to the extent of corrosion and microfouling of toxic surfaces from tropical waters is scanty. In view of this, an effort has been made to establish relationship between the extent of microfouling and corrosion rate of copper and its alloys in natural environment. A station on the southern west coast of India was selected for the purpose. The data on corrosion and microfouling have been collected for three different seasons and discussed.

### Experimental Procedure

Panels admeasuring  $8 \times 5$  cm of commercial grade copper (Ni-0.05%, Cu-rest), cupronickel 90/10 (Fe-0.8%, Ni-8.6%, Cu-rest) and cupronickel 70/30 (Fe-0.5%, Ni-26.8%, Cu-rest) were cleaned prior to deployment by following standard methods<sup>10</sup>. These panels were weighed accurately upto four decimals and then deployed in seawater at New Mangalore Port, which is situated on the southern west coast of India (Fig. 1). The panels were fixed on fibreglass strips with PVC nut and bolts. The panels were deployed during beginning and retrieved at the end of each season. The investigation was carried out for postmonsoon (October 1992-January 1993), premonsoon (February 1993-May 1993) and monsoon (June 1993-September 1993). The panels were studied in six replicates.

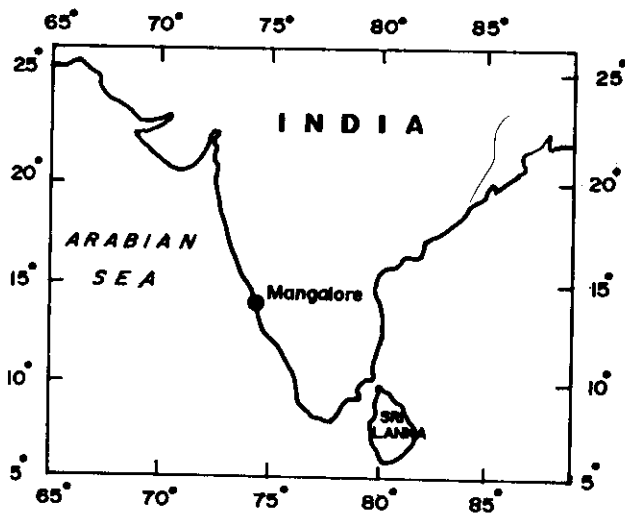


Fig. 1—Station location map

After retrieval the panels were first rinsed gently with sterile seawater to remove any non-adhering bacteria and diatoms. The fouled matter was scraped with nylon brush<sup>11</sup> in sterile seawater of known volume. One millilitre of the scraped material was used immediately for bacterial count (viable). The balance was preserved with Lugol's KI-I<sub>2</sub> solution. The preserved material was then subjected to sedimentation in a settling chamber<sup>12</sup> and the phytoplankton cells were enumerated under inverted microscope. Panels were studied in triplicate for diatom and bacterial count and the average values are plotted.

Another set of three fouled panels were utilized for extraction and estimation of exopolysaccharides (EPS) from the biofilm. The biofilm was removed by scraping the surface of the panels with nylon brush in 1 M NaCl solution<sup>8,13</sup>. The scraped material was made to known volume. It was filtered through ashed (450°C) glass fibrefilters (GF/C). The filtrate was then used for the estimation of EPS using the phenol-sulphuric acid method<sup>14</sup>.

Immediately after scraping off the biofilm from both the sets of panels, they were then cleaned by following standard method<sup>10</sup> and weighed after desiccation. The difference between initial weight prior to deployment and final weight was used for calculation of corrosion rate by using the following formula:

$$mdd = W/(A \times T)$$

where *mdd* is corrosion rate expressed in terms of metal loss (mg) per decimetre square area per day, *W* is loss in weight (mg), *A* is area of panels (dm<sup>2</sup>), and *T* is exposure time (days).

The scraped corrosion product was subjected to X-ray diffraction (XRD) analysis for qualitative

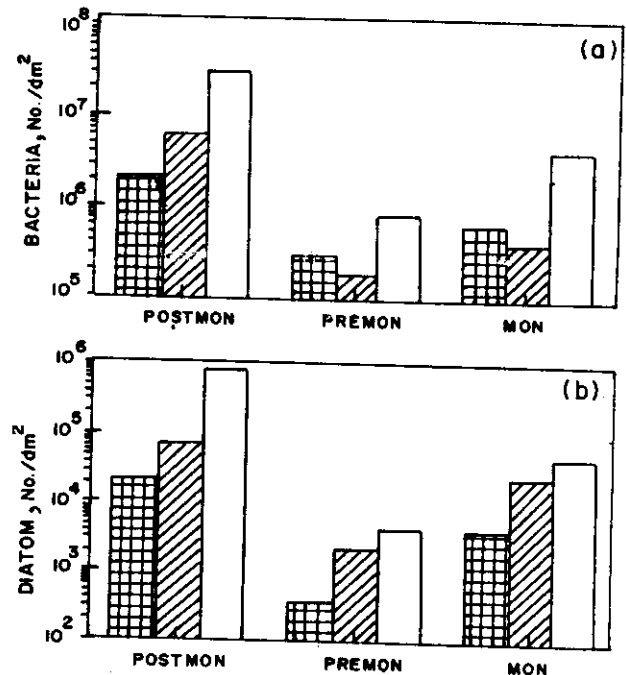


Fig. 2—Seasonal variations in the bacterial (viable) (a) and diatom (b) counts of biofilm on copper ■, cupronickel 90/10 ▨ and cupronickel 70/10 □

estimation of compounds. The intensities were compared with powder diffraction analysis data and identified.

## Results and Discussion

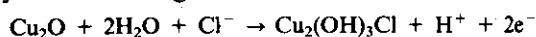
Panels of copper, cupronickel 90/10 and cupronickel 70/30 were found to remain free from macrofoulers for all the three seasons. However, the panels were fouled by microfouling assemblage of varying extent. The extent and nature of microfouling assemblage varied with the type of surface and the season of exposure.

In general, the microfouling biomass was higher on cupronickel 70/30 as compared with other two surfaces. Seasonal variations in the extent of microfouling were evident (Figs 2, 3). As regards the exopolysaccharide content of the biofilm, it was high during monsoon and low during premonsoon (Fig. 3b). Exopolysaccharide content was higher on cupronickel 70/30 as compared with other two surfaces. Bacterial cells were maximum during postmonsoon and minimum during premonsoon (Fig. 2a). Marked differences to the extent of settlement of bacteria was observed with substrata. Cupronickel 70/30 was fouled more by bacterial cells than the other two surfaces under study. Similar results were also observed in case of diatom numbers (Fig. 2b). The diatom population was more diverse during monsoon as compared to rest of the period (Table 1). Total nine forms were encountered during

the period of study. These forms were *Acnantes* sp., *Pleurosigma* sp., *Nitzschia* sp., *Navicula* sp., *Fragilaria* sp., *Biddulphia* sp., *Thalasiothrix* sp., *Chaetoceros* sp. and *Amphora* sp. Among these forms *Navicula* sp. was conspicuous during all the three seasons (Table 1).

As regards the corrosion of copper and its alloys under study the rate for the copper, cupronickel 90/10 and cupronickel 70/30 were found to vary between 11-15.4, 9.8-14.2 and 4.2-5.0 mdd respectively. The corrosion rates for all the three materials were found to vary with the season. The corrosion rates were higher during premonsoon as compared to rest of the

periods. It is evident from the data that the corrosion rate varied with type of materials. The corrosion rates of copper and cupronickel 90/10 were nearly 3 times higher than that of cupronickel 70/30, suggesting that cupronickel 70/30 is more resistant to seawater exposure. The resistivity of these metal and alloys to seawater exposure decreased in the order as, cupronickel 70/30 > cupronickel 90/10 > copper. Thus the metal and alloys under study exhibited decreasing trend of corrosion rate with increased nickel content. These observations are in well agreement with those reported by Chauhan and Gadiyar<sup>15</sup>. Visual observations made at the corroded layer of the panels showed two distinct layers of the corrosion product. The outer layer was dark green and the inner was brown. The XRD analysis of the corrosion product revealed presence of  $\text{Cu}_2\text{O}$  as the major component in the inner layer, whereas the outer layer indicated presence of atacamite. The amount of  $\text{Cu}_2\text{O}$  appeared to be higher in case of Cu-Ni 90/10 which is the characteristic of the alloy. Normally in Cu-Ni alloys  $\text{Cu}_2\text{O}$  film dopes with alloying elements which in turn offers higher protection to the alloy. It has been hypothesised that the inner  $\text{Cu}_2\text{O}$  layer gets oxidised to form atacamite by the following reaction:



The present investigation showed inverse relationship between corrosion rate and some of the microfouling parameters under study. The extent of microfouling assemblage decreased on copper and increased on cupronickel 70/30. It is well evident that the rate of corrosion influenced the extent and nature of fouling. The higher the resistivity of the metals to seawater corrosion, lower is the resistance to fouling organisms and vice versa. Therefore, the resistivity of

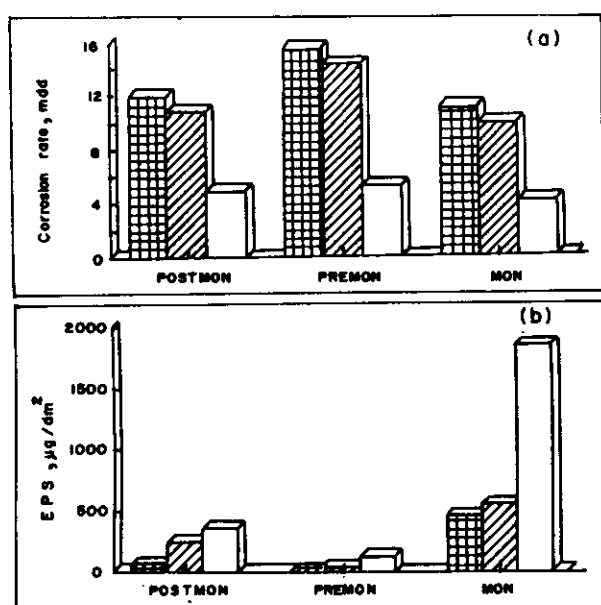


Fig. 3—Seasonal variations in the extent of corrosion (a) and EPS content (b) of biofilm on copper ■, cupronickel 90/10 ▨ and cupronickel 70/30 □

Table 1—Seasonal variations in the extent ( $\text{No}/\text{dm}^2$ ) and nature of fouling diatoms on copper and its alloy surfaces

Diatom sp.	Post-monsoon			Pre-monsoon			Monsoon		
	1	2	3	1	2	3	1	2	3
<i>Acnantes</i> sp.	—	—	21923	—	—	—	1930	1144	35990
<i>Pleurosigma</i> sp.	—	—	—	—	—	37	429	—	8115
<i>Nitzschia</i> sp.	—	—	5769	47	—	37	858	12392	4587
<i>Navicula</i> sp.	20470	59607	651922	329	2263	2737	214	12293	307
<i>Fragilaria</i> sp.	—	—	—	—	—	—	214	381	1940
<i>Biddulphia</i> sp.	—	—	—	—	—	—	214	381	—
<i>Thalasiothrix</i> sp.	—	—	—	—	—	—	—	—	352
<i>Chaetoceros</i> sp.	—	—	—	—	—	—	858	953	1009
<i>Amphora</i> sp.	3594	13594	123461	—	—	1698	—	—	—

1 = Copper; 2 = Cupronickel (90/10); 3 = Cupronickel (70/30)

copper and its alloys towards fouling depends on corrosion rate in the natural environment<sup>9</sup>. Reportedly leaching rate of copper greater than 10  $\mu\text{g}/\text{cm}^2/\text{day}$  can prevent fouling<sup>9</sup>. This rate of leaching is prescribed for macrofouling organisms. The corrosion rates of copper and its alloys under study were 4-11 times higher than the prescribed leaching rate of copper. It is presumed that due to this reason the copper and its alloys under study remained free from macrofoulers. It is believed that copper ions are slowly released in seawater from copper surface as a result of corrosion and they poison the free swimming or settling stages of macrofoulers<sup>16,17</sup>. According to Efir<sup>18</sup>, Crisp and Austin<sup>19</sup> and Dewolf<sup>20</sup> the fouling resistance of copper is not only because of leaching but it is also due to cuprous oxide corrosion product that is toxic to the settled organisms.

Though the leaching rate of copper for control of macrofouling is specified, the same is not applicable to the control of microfouling. This is because some of the species of bacteria and diatoms of the microfouling community possess resistance to toxicity of copper ions. The mechanisms involve production of copious mucilage which encapsulates the cells<sup>21</sup>. It has been shown that diatoms and bacteria subjected to high concentrations of heavy metals release large quantity of organics which interact with metal ions<sup>22</sup>. Stanbury<sup>23</sup>, however, implicated some form of intracellular immobilization or chelation and Bishop *et al.*<sup>24</sup> also implied an internal system regarding the chloroplasts as a suitable site for chelation. Hardstedt-Romeo *et al.*<sup>25</sup> have provided evidence on the complexation of copper with phytoplankton exudate. All these studies provide evidence on the development of resistance towards toxic metal surfaces by the microfouling community.

As regards EPS of biofilm, its chemistry has been tried by many. Exopolysaccharides are usually acidic heteropolysaccharides. Functional groups such as hydroxyl, carboxyl and phosphoric acids associated with EPS exhibited a high affinity towards different types of dissolved organic and certain metal ions<sup>26,27</sup>. The involvement of such functional groups of EPS in microfouling and biocorrosion processes have been demonstrated by using various techniques<sup>27-29</sup>. It has been reported that EPS such as alginates produced by algae and bacteria are negatively charged and rich in uronic acids. Such EPS exhibit high metal complexing capacity<sup>30</sup>. Algal EPS containing high uronic acid exhibit high copper binding capacity<sup>31</sup>. In one of our earlier studies it was observed that uronic acid content was significant in EPS produced by *Navicula subinflata*<sup>8</sup>. In the present

investigation, the incidence of the diatom species of *Navicula* was conspicuous in the biofilm and might have contributed to some extent to the production of EPS. All these points suggest that microfouling community and its EPS on copper and its alloys can lead to reduction of corrosion rate by virtue of forming a protective film over the surfaces. The inverse relationship between microfouling parameters and the corrosion rates of the metals and alloys under study could be explained on the above mentioned points. The data on EPS when compared with fouling biomass exhibited very poor correlation with the data on bacterial count. The possible explanation is that the environmental stresses which are believed to be the controlling factors for the production of EPS might be the causative factor for this differences<sup>8</sup>.

It is evident from the present study that the corrosion rate of copper alloys decreases with increase of nickel content as alloying element. The ability of the metal and its alloys under study to get fouled in natural seawater increases in the order as Cu < Cu-Ni, 90/10 < Cu-Ni, 70/30. Inverse relationship was evident between the extent of microfouling and EPS and diatom. Poor correlation between bacterial count and corrosion rate suggest that the corrosion rate is more controlled by EPS than the bacterial cell numbers.

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