

Corrosion behaviour of copper in mandapam seawater

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The corrosion characteristics of copper were investigated in the palk bay waters of the Mandapam coast, India over a period of a year. This work comprises both field exposure as well as laboratory studies. The experimental method included determination of corrosion rate by weight loss measurement and analysis of the corrosion products by x-ray diffraction. The XRD analysis of the products on copper threw more light on the nature of the oxide film formed and their impact on the overall corrosion rate/bio fouling of the material. The effect of biofilm on corrosion behaviour of copper was investigated by Tafel polarization and impedance techniques. The annual (oct'96-sep'97) corrosion rate of copper was 0.045 mmpy with no fouling.

Keywords: Biofouling, Corrosion, Impedance, Polarization, Copper, Seawater

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Copper alloys find application in a wide variety of marine environments¹. Copper alloys have a long history of successful application in the marine environment because of their corrosion resistance, mechanical workability, excellent conductivity, ease of soldering and brazing, and resistance to macro fouling². Copper corrodes at negligible rates in unpolluted air, water and deaerated non-oxidizing acids. Copper alloys resist many saline solutions, alkaline solutions and organic chemicals. However, copper is susceptible to more rapid attack in oxidizing acid, oxidizing heavy metal salts, sulphur and ammonia.

The corrosion behaviour of copper alloy is detrimental to biofouling. Long-term exposure of copper and its alloys in the ocean has indicated that marine organisms are generally prevented from causing damage in its presence³. Generally, copper and its alloys are toxic to the fouling organisms and they function by slowly releasing copper ions into the aqueous environment, which poisons the growth of fouling organisms⁴.

In this paper, the corrosion behaviour of copper in Palk Bay waters of Mandapam and the nature of the corrosion products formed on it, are reported.

Experimental Procedure

Field exposure details

Mandapam (longitude 79° 8' east, Latitude 9° 17' north) is a tropical marine environment where South-

West and North-East monsoons influence the weather as well as the nature of fouling⁵. Southwest and the northeast monsoons prevailing during the period April to August and November to February respectively influence climate in Mandapam. The present studies were conducted in the Palk Bay waters of Mandapam, for a period of one year. Commercially available 3 mm thick sheets of copper were cut into test panels of size 150 × 50 mm. The samples were polished, degreased and weighed to an accuracy of ± 0.1 mg and fixed in conventional wooden racks with brass bolt and nuts. Metal to metal and metal to wood contacts were prevented by using polythene insulators. The racks were immersed in sea below the mean low tide level in the Palk Bay of Mandapam.

Laboratory studies

Copper coupons of size 5 × 2 cm were taken, polished and weighed to an accuracy of 10⁻⁴g. For fouling experiments, duplicate coupons of copper were exposed in Palk Bay seawater for 3 and 6 months. Another set was immersed in sterilized seawater medium in the laboratory. The natural seawater used for microfouling experiments in the laboratory was renewed with fresh seawater once in 48 h.

For data collection, samples were exposed or withdrawn in duplicate. The gravimetric corrosion rates were calculated after experimentation in natural seawater and sterilized seawater were cleaned in the recommended cleaning solutions⁶.

The surface temperature of the seawater was measured using a standard centigrade thermometer. The major ions present in the seawater such as chloride, sulphate, carbonate, bicarbonate, calcium and magnesium were estimated during the study period using appropriate techniques⁷ and the dissolved oxygen concentration was measured using the iodimetric method⁸. Table 1 gives the seawater characteristics.

Electrochemical studies

Electrochemical DC measurements were made as a function of exposure time for metals in natural and sterilized seawater, with the PAR173 Potentiostat, PARC 175 Universal programmer and HP 7004B X-Y recorder or by using Electrochemical system (solarton1280B). Electrochemical measurements were made using 1 cm² specimen at a sweep rate of 1 mV/s. Anodic and cathodic Tafel slopes (b_a and b_c), corrosion current density (i_{corr}) and corrosion potential (E_{corr}) were derived from the E versus $\log i$ plots.

Electrochemical impedance spectroscopy (EIS) data were collected for copper surface in natural and sterilized seawater for different periods of immersion. Impedance spectra were obtained with 6310 Impedance analyzer (EG&G Instruments Princeton Applied Research) for the frequency range of 1 mHz to 10 KHz under stationery conditions at $30 \pm 1^\circ\text{C}$. Both DC polarization and EIS measurements were carried out in a 3-electrode cell consisting of working electrode, platinum auxiliary electrode and saturated calomel electrode.

Results and Discussion

Figure 1 illustrates the monthly corrosion rate of copper in field condition of Mandapam Palk Bay water. The monthly corrosion rate value of copper is in the range of 0.07 to 0.21 mmpy and there is no macro or micro fouling organisms on copper surfaces throughout the study period. A higher value of corrosion rate is observed during initial exposure period of Dec'96. After Dec'96 the corrosion rates were very less upto sep'97. The maximum value of corrosion rate during Dec'96 could be attributed to the removal /breakdown of oxide film by turbulent wave actions⁹. Southwest and the northeast monsoons prevailing during the period April to August and November to February respectively influence climate in Mandapam. For instance the sea at Palk Bay is rough during northeast monsoon where as the one at Gulf of Mannar becomes calm. The reverse happens

when southwest monsoon takes over. It is quite well known that there is no fouling formation on the metal surface due to the selective leaching of toxic ions from the copper matrix.

Figure 2 illustrates the corrosion rate for cumulative exposure of copper in natural seawater namely three, six, nine and 12 months. The steady decline in the corrosion rate values with longer duration of exposure is attributed to the formation of protective nature of corrosion products¹⁰. In terms of

Table 1—Sea water characteristics

No	Characteristics	Maximum	Minimum	Average
1	Surface temperature, °C	31.2	26.4	28.8
2	Salinity, ppt	35.0	25.6	30.3
3	Dissolved oxygen, mL/L	5.0	2.8	4.2
4	Calcium, mg/L	332	329	331
5	Magnesium, mg/L	1173	1158	1166
6	Carbonate, mg/L	20.5	15.4	18.0
7	Bicarbonate, mg/L	115	105	110
8	Sulphate, mg/L	2165	2153	2159
9	pH	8.3	8.1	8.2

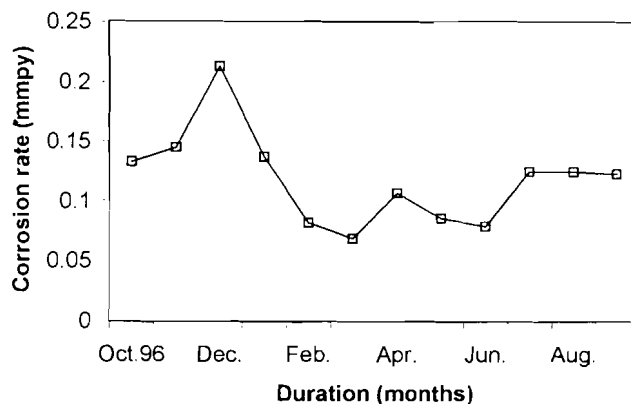


Fig. 1—Monthly corrosion rate of copper in natural seawater

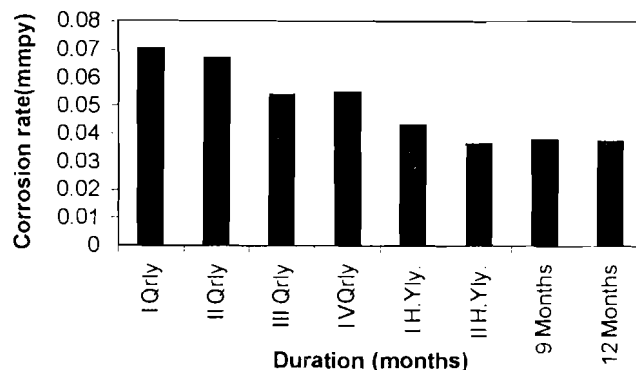


Fig. 2—Cumulative exposure of copper in natural seawater

corrosion rate, Ist quarterly (oct'96-Dec'96) exposure has experienced higher corrosion rate than other quarterly exposure periods. It is also observed that after one year exposure, the copper surface experienced insignificant fouling during the study period.

Maruthamuthu *et al.*¹¹ have reported that the corrosion rate of copper in natural seawater is 0.087 mmpy in Tuticorin harbour water and at Panama Canal Zone the rate of corrosion of copper was 0.0051 mmpy¹². It is found that the corrosion rate of copper in Mandapam water is 0.045 mmpy. Figures 3-5 show XRD data of copper corrosion products in natural seawater. It is quite evident that Cu₂O is the most important product as indicated by the strongest peak at 2θ = 36.3° corresponding to the *d* values of 2.3747. This line is finger print of Cu₂O with maximum relative intensity. The complete set is present in the XRD pattern confirming the presence of Cu₂O in the corrosion product. Further, from the intensity of the line one can infer that it is not only the first product which is formed on copper coupons and grows in intensity with time but also it gets converted into other products like hydroxide, copper carbonate, oxy chloride etc. Table 2 summarizes the XRD results. It is observed from the table that initially the corrosion product is Cu₂O and CuCl₂. As the exposure period is increased, the inherently fouling resistant material is subsequently oxidized to CuCl₂. 3Cu(OH)₂ does not appear to be toxic to marine organisms. The CuCl₂.3Cu(OH)₂ periodically sloughs off from the material surface. This re-exposes the adherent toxic Cu₂O film and renews the fouling resistance.

Table 3 summarizes the corrosion rate values obtained for copper by weight loss method in both the media for the exposed period of 3 months and 6 months respectively. The rate of corrosion of copper in natural seawater is high compared to sterile

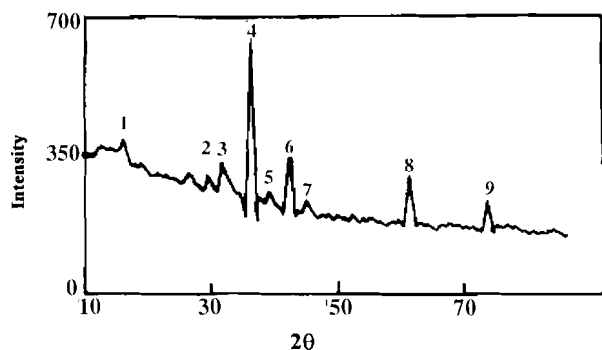


Fig. 3—XRD pattern on corrosion products of copper in natural seawater-3 months

seawater immersion. The corrosion rate is decreased with exposure time in natural seawater. Table 4 gives the corrosion rate values obtained by polarization method. The corresponding polarization curves obtained for copper in natural seawater and sterilized seawater are shown in Figs 6 and 7, respectively.

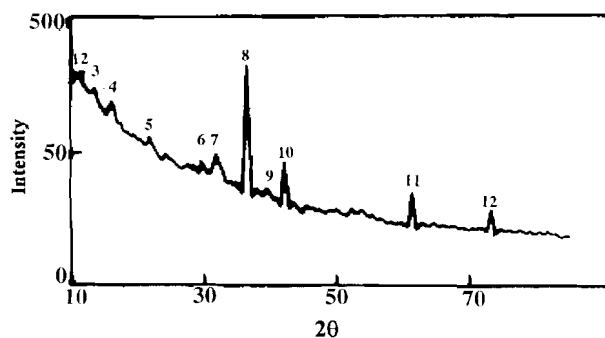


Fig. 4—XRD pattern on corrosion products of copper in natural seawater-6 months

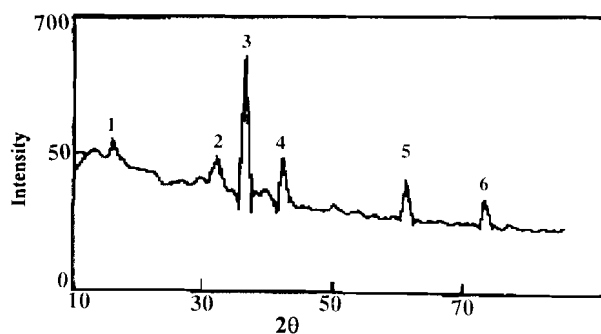


Fig. 5—XRD pattern on corrosion products of copper in natural seawater-12 months

Table 2—XRD Data on corrosion products of copper in natural seawater

No	Period of exposure	Composite corrosion products
1	Monthly	Cu ₂ O, CuCl ₂
2	Quarterly	Cu ₂ O
3	Half yearly	Cu ₂ O
4	Yearly	CuO, Cu ₂ O

Table 3—Comparison of corrosion rate values for copper obtained by gravimetric method

S.No	Duration (months)	Corrosion rate, mmpy	
		Natural sea water	Sterile sea water
1	3	0.0613	0.0207
2	6	0.0433	0.0338

From the data it is observed that i_{corr} value for 3 months period of exposure in natural seawater is $23 \mu\text{A}\cdot\text{cm}^2$, whereas in the sterilized seawater the i_{corr} value is $3 \mu\text{A}\cdot\text{cm}^2$. The loosely adherent corrosion product formation in natural seawater exposure favours higher corrosion rate, whereas an adherent corrosion product layer formed in sterilized seawater reduces the corrosion rate. As the duration of exposure is longer, the i_{corr} value decreases to $7 \mu\text{A}\cdot\text{cm}^2$ in natural seawater. However, the i_{corr} values of copper in sterile seawater remained unaffected with exposure time.

Table 4—Polarization parameters for copper in natural seawater and sterile seawater

Medium	S. No	Duration (months)	E_{corr} (mV vs SCE)	i_{corr} ($\mu\text{A}/\text{cm}^2$)	b_a (mV)	b_c (mV)	Corrosion rate, mmpy
NSW	1	3	-315	23	124	146	0.5231
	2	6	-388	7	74	92	0.1592
SSW	1	3	-310	3	100	66	0.0682
	2	6	-298	5	70	76	0.1137

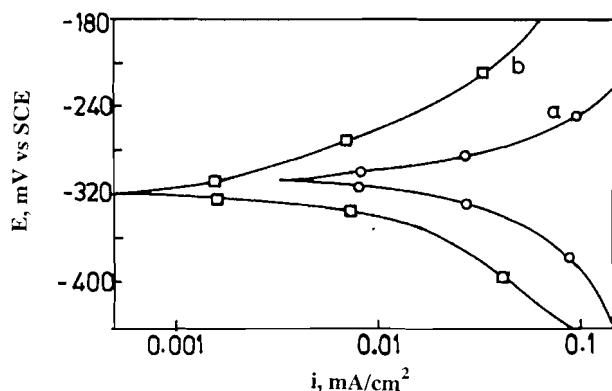


Fig. 6—Polarization behaviour of copper (a) in natural seawater (b) in sterilized seawater (3 months)

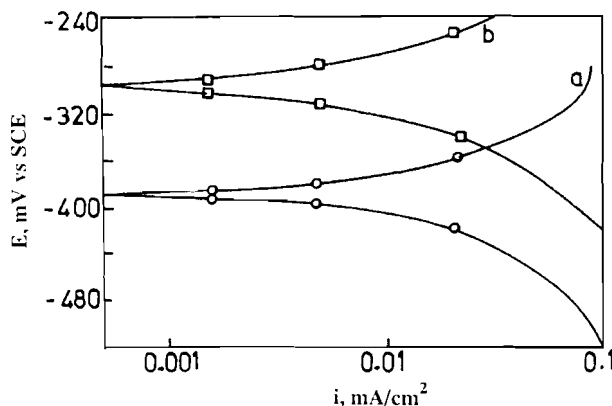


Fig. 7—Polarization behaviour of copper (a) in natural seawater (b) in sterilized seawater (6 months)

The impedance behaviour of copper in natural seawater and sterilized seawater are shown in Figs 8-11. It is found from the figures that the charge transfer value (R_t) in natural seawater exposure (3 months) of copper is $40 \text{ ohm}\cdot\text{cm}^2$. But in sterile seawater immersion, the R_t value has increased to

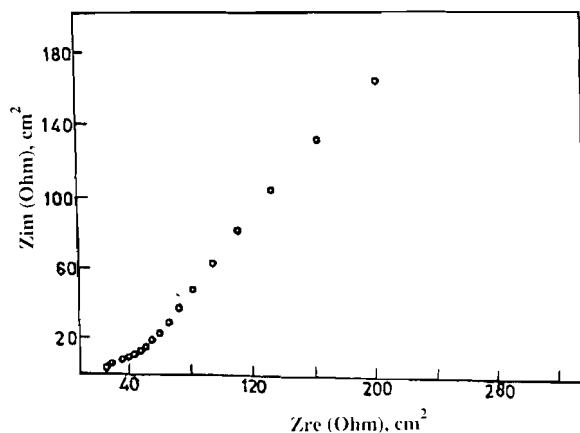


Fig. 8—Impedance behaviour of copper in natural seawater (3 months)

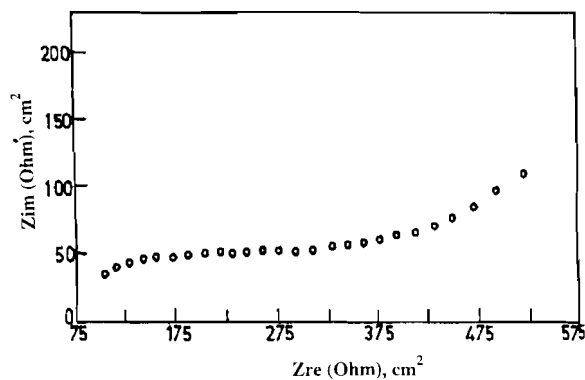


Fig. 9—Impedance behaviour of copper in sterile seawater (3 months)

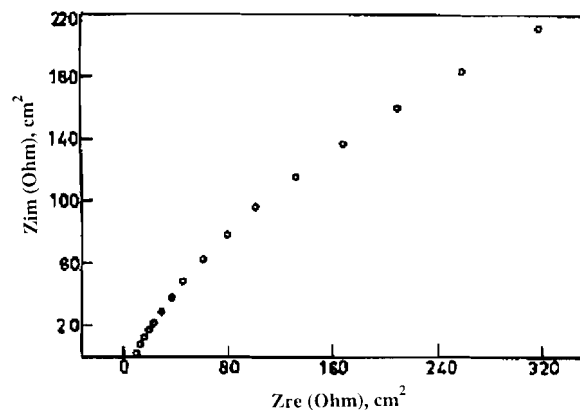


Fig. 10—Impedance behaviour of copper in natural seawater (6 months)