MICROBIOLOGICALLY INDUCED CORROSION OF COPPER

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ABSTRACT

Corrosion and microfouling studies on copper were carried out in pond water and mixed culture of *Pseudomonas* sp., *Vibrio* sp. and *Bacillus* sp. The effect of biofilm in natural and mixed culture on corrosion of copper has been found out by various methods like weight loss, polarization and impedance measurement for an exposure period of 100 days. Less corrosion current and high resistance values were observed for copper in pond water biofilm and mixed culture biofilm. The nature of the corrosion products in the presence of biofilm has been identified by XRD analysis. XRD data show broad peaks obtained in the presence of natural biofilm, indicating that the films are made up of organic compounds. The results suggest that bacterial activity inhibits the corrosion of copper.

Key words: Copper, Biofilm, Corrosion inhibition, *Pseudomonas* sp., *Vibrio* sp. and *Bacillus* sp.

INTRODUCTION

Copper and its alloys have a long history of successful application in the marine environment. For many years, research on biocorrosion focused only on sulphate-reducing bacteria (SRB) /1-5/. Recently, it has become evident

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that several other organisms also induce corrosion /6/. Corrosion of iron and nickel was increased in the presence of *Pseudomonas* sp. and *Serratia marcescens* sp. /7/. But a protective effect of these species was found when applied as sense suspensions ($10^9 ml^{-1}$) /7,8/. The *Pseudomonas fragi* and *Escherichiocoli* protected steel only when present as living biofilm /9,10/. Engineered protective biofilm, secreting anti-microbial proteins active against corrosion-causing sulfate reducing bacteria (SRB), were shown to reduce the corrosive attack of stainless steel by these deleterious bacteria /11/. However, the influence of copper-tolerating microorganisms on corrosion control of copper in fresh water has not been thoroughly studied. The aim of this study is to determine the conditions responsible for the observed decrease of corrosion of copper.

EXPERIMENTAL APPROACH

Copper coupons of purity 99.9% and size 100 × 100, 2mm specimens were polished with 240 grit paper, degreased, weighed and exposed to natural pond water system, a mixed culture system of *Pseudomonas* sp., *Vibrio* sp. and *Bacillus* sp., and an abiotic system for a period of 100 days. Specimens of 1 cm^2 area were used for the electrochemical studies. The natural pond water was changed at every 24-hour intervals in order to make the biofilm alive. The same water was sterilized by autoclaving at 120 °C for 15 to 20 minutes. This sterilized water was used as a control medium (without bacteria). The co-culture of *Pseudomonas* sp., *Vibrio* sp. and *Bacillus* sp. was used for the mixed culture system. A nutrient broth alone was used for the control of the mixed culture system.

These studies were carried out by immersion test as recommended in ASTM standard G 31-36. At frequent intervals the corrosion rates of copper coupons were determined.

Tafel polarization measurements were carried out potentiodynamically using a Potentiostat (PAR model 173) in conjunction with a potentioscan generator (PAR 175) and an XY recorder (Rikdenky Model R206) employing a stationary electrode. The electrode potential was fixed at 200 mV cathodic to open circuit potential (OCP) and allowed to attain a steady state value. The steady state polarization was carried out from –200 mV to +200 mV w.r.t. the OCP at a scan rate of 0.5 mV/sec. The i_{corr} values were obtained from the plots of E vs log i curves. The impedance studies were carried out using computer controlled EG & G electrochemical impedance analyzer (model M 6310) with software M 398. After attainment of a steady state potential, AC signal of 10 mV amplitude was applied and impedance values were measured for frequencies ranging from 0.01 Hz to 10 KHz. The values of R_t were obtained from the Nyquist plots.

The specimens were dried and the surface film was analyzed by X-ray diffraction. The XRD pattern was recorded using computer-controlled XRD system, Jeol (Japan) model JDX – 8030 with CuK α radiation (Ni-filtered = 1.5418 Å) at a rating of 40 kV. The 'peak search' and 'search match' programmes (built in software) were used to identify the peak table and ultimately for identification of the XRD peaks.

RESULTS AND DISCUSSION

The biological characteristics of the system are given in Table 1. The bacterial counts of heterotrophic bacteria in natural pond water were about 6.5×10^2 to 7.5×10^4 CFU/cm^2 and those in the mixture culture system were 5.5×10^3 to 8.5×10^3 CFU/cm^2. This shows that attachment of copper tolerating bacteria takes place on copper. The potentials were on the more positive side in the natural pond water and mixed culture system. The remarkable protective effect of the biofilm cannot be due solely to a reduction of the oxygen concentration on the copper surface in the presence of the biofilm, since the corrosion potential E_{corr} was found to increase with time, i.e., the ennoblement of copper was observed in the presence of a bacterial biofilm (Figs. 1 and 2).

The weight loss data indicate that the corrosion rates of copper in the presence of natural pond water biofilm and mixed culture biofilm were less in the range of 0.0020 mmpy to 0.0065 mmpy (Table 2). But in the abiotic system, the corrosion rates were very high during their immersion period. *Pseudomonas fragi* and *Escherichiocoli* were found to reduce the corrosion of steel only when present as living biofilm /9,10/. The electrochemical polarization study indicated that the corrosion rates were less in natural pond water biofilm and mixed culture biofilm in the range of 1.7×10^{-6} mmpy to 4.0×10^{-6} mmpy. But in the control system the corrosion rates were in the range of 2.1×10^{-5} mmpy to 12×10^{-5} mmpy during the study period (Table 3). Impedance behavior of copper exposed to natural pond water, mixed culture system and its control system is shown in Fig. 3a and 3b, Fig. 4a and

Table 1

Biological characteristics of biofilm, pH and dissolved oxygen values of natural pondwater system and mixed culture system

Days	Bacterial Density in natural pond water (CFU/cm^2)	Bacterial Density in mixed culture system (CFU/cm^2)	pH	DO (ppm)
10	6.5 x 10^3	6.0 x 10^4	7.0 to 7.1	4.86 - 4.99
20	6.5 x 10^2	7.0 x 10^2	7.2 - 7.3	4.92 - 5.01
40	5.5 x 10^3	5.5 x 10^3	7.1 - 7.2	4.81 - 4.99
60	8.0 x 10^3	8.5 x 10^3	7.0 - 7.3	4.75 - 4.87
80	7.5 x 10^4	6.5 x 10^5	7.1 - 7.0	4.64 - 4.98
100	8.2 x 10^3	6.5 x 10^4	7.1 - 7.2	4.92 - 5.00

Table 2

Corrosion rates of copper in natural pond water system, mixed culture system and abiotic system obtained by weight loss method

Days	Corrosion Rates - mmpy		Corrosion Rates - mmpy	
	Natural pond water	Control	Mixed culture system	Control (3% nutrient only)
10	N.D.	N.D.	N.D.	N.D.
20	0.0020	0.0102	0.0030	0.0060
40	0.0025	0.015	0.0045	0.0071
60	0.0022	0.0120	0.0052	0.0105
80	0.0027	0.0125	0.0065	0.0115
100	0.0037	0.0350	0.0062	0.0135

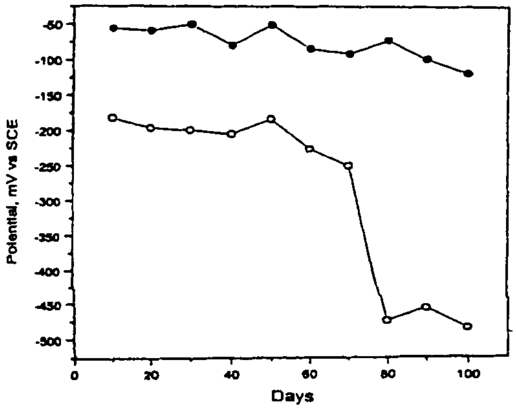

Fig. 1: Potential of copper in pond water system and in control
--O-- Control
--●-- Pond water system

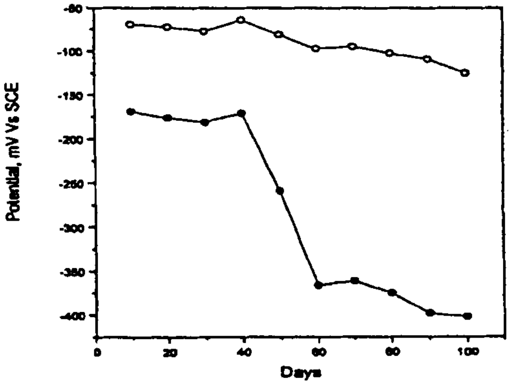

Fig. 2: Potential of copper in mixed culture system and in control
--O-- Mixed culture system
--●-- Control

4b and the impedance parameters are given in Table 4. The charge transfer resistance values in the natural pond water system and mixed culture system have been slowly increased from 51 Kohm.cm^2 to 342 Kohm.cm^2. But in the control system the R_t values were less than 72 Kohm.cm^2 during their

Table 3

Corrosion rates of copper in natural pond water system, mixed culture system and abiotic system by polarization technique

Days	Natural pond water system		Control		Mixed culture system		Control (3% nutrient only)	
	I_{corr} (μA/cm^2)	Corr. rate (mmpy)	I_{corr} (μA/cm^2)	Corr. rate (mmpy)	I_{corr} (μA/cm^2)	Corr. rate (mmpy)	I_{corr} (μA/cm^2)	Corr. rate (mmpy)
10	0.015	1.7×10^{-6}	0.11	1.2×10^{-5}	0.0068	7.5×10^{-7}	0.13	1.4×10^{-5}
30	0.022	2.4×10^{-6}	0.13	1.4×10^{-5}	0.012	1.3×10^{-6}	0.16	1.2×10^{-5}
60	0.035	3.7×10^{-6}	0.16	1.8×10^{-5}	0.02	2.2×10^{-6}	0.16	1.8×10^{-5}
100	0.084	9.5×10^{-6}	0.19	2.1×10^{-5}	0.036	4.0×10^{-6}	0.19	2.1×10^{-5}

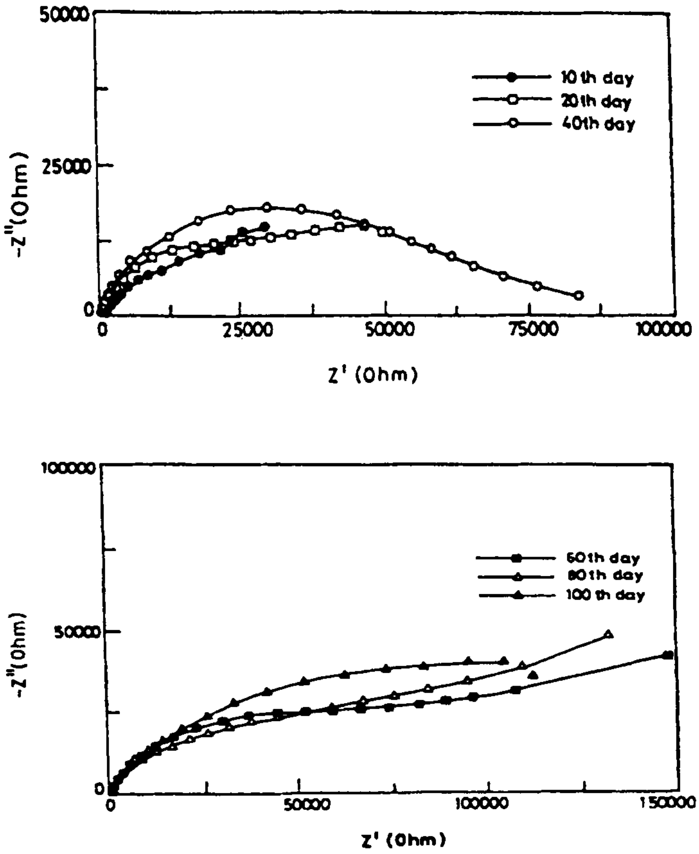

Fig. 3a: Impedance plots for copper in natural pond water system.

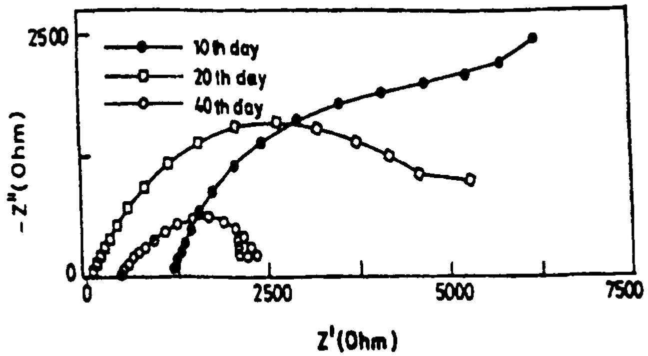

Fig. 3b (continued)

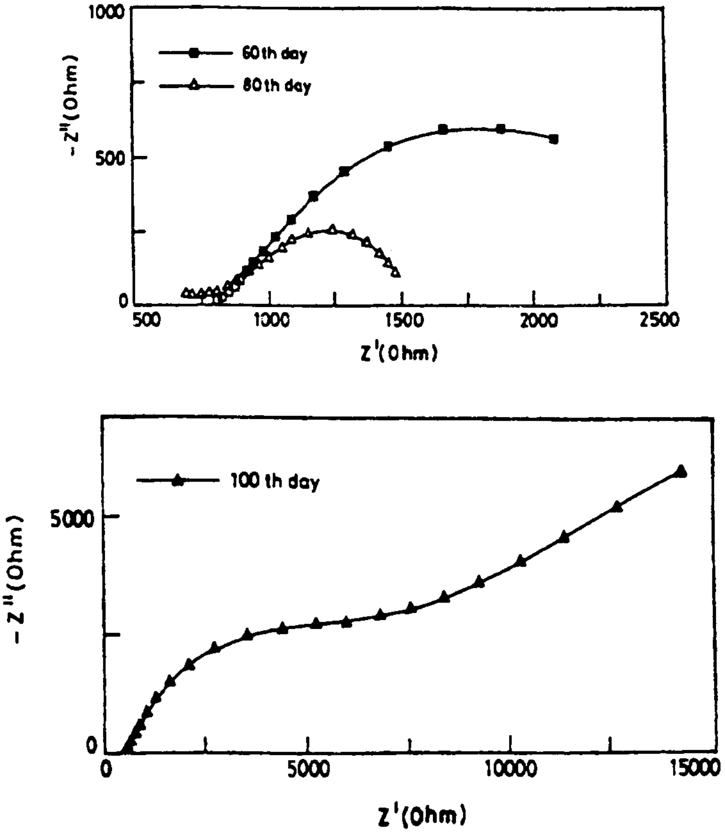

Fig. 3b: Impedance plots for copper in control system.

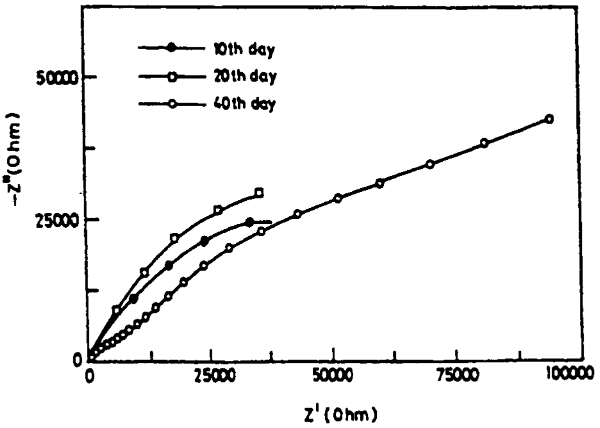

Fig. 4a (continued)

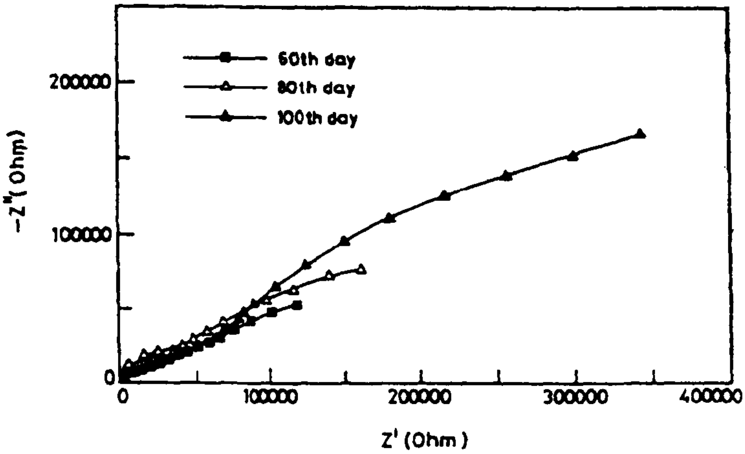

Fig. 4a: Impedance plots for copper in mixed culture system.

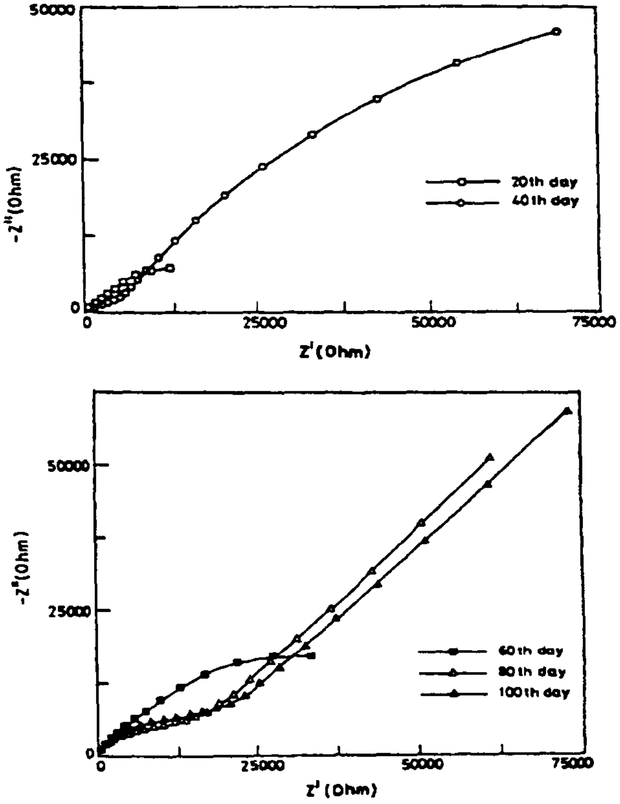

Fig. 4b: Impedance plots for copper in control system.

Table 4

Impedance parameter for copper in natural pond water system, mixed culture system and abiotic system

Days	Natural pond water system		Control		Mixed culture system		Control (3% nutrient only)	
	R_t (Kohm.cm^2)	Cdl (F/cm^2)	R_t (Kohm.cm^2)	Cdl (F/cm^2)	R_t (Kohm.cm^2)	Cdl (F/cm^2)	R_t (Kohm.cm^2)	Cdl (F/cm^2)
10	51.00	7.776^{e-5}	8.01	1.373^{e-4}	37.28	6.113^{e-5}	49.23	3.043^{3-5}
20	70.16	9.842^{e-6}	5.21	4.688^{e-4}	39.74	60.27^{e-5}	1.88	8.905^{e-5}
40	80.40	5.694^{e-6}	2.14	6.70^{e-3}	94.03	1.764^{e-5}	68.64	2.425^{e-5}
60	115.43	8.051^{e-6}	12.82	1.561^{e-4}	118.49	1.334^{e-5}	33.63	4.721^{e-5}
80	158.35	9.902^{e-2}	0.78	648^{e-3}	160.27	8.898^{e-5}	61.01	2.192^{e-5}
100	165.51	1.046^{e-5}	14.11	6.424^{e-5}	342.39	4.891^{e-5}	72.68	1.853^{e-5}

immersion period. The reason for the reduced corrosion rate in the presence of biofilm is due to limited diffusion of oxygen and corrosive agents through biofilm /12/.

Corrosion inhibition of mild steel by different aerobic bacteria, *Rhodococcus* sp., *Pseudomonas putida* and *Streptomyces pilosus* in corrosive aqueous medium was reported /13/. Pitting corrosion control by using regenerative biofilm on aluminium 2024 in artificial seawater has been reported /14/. Engineered protective biofilm, secreting antimicrobial proteins active against corrosion-causing sulfate-reducing bacteria (SRB), was shown to reduce the corrosive attack of stainless steel by these deleterious bacteria /15/. In the XRD analysis (Figs. 5 and 6), broad organic peaks were obtained in the natural pond water biofilm and mixed culture biofilm, but in the abiotic

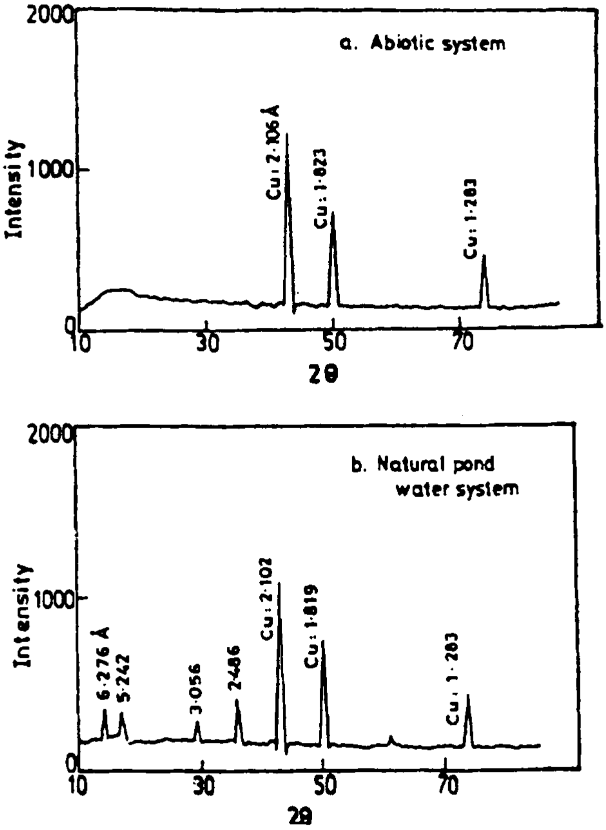

Fig. 5: XRD pattern of corrosion product of copper in natural pond water system and control.

system, only copper peaks were identified. This indicates the formation of organometallic complex on copper for protection.

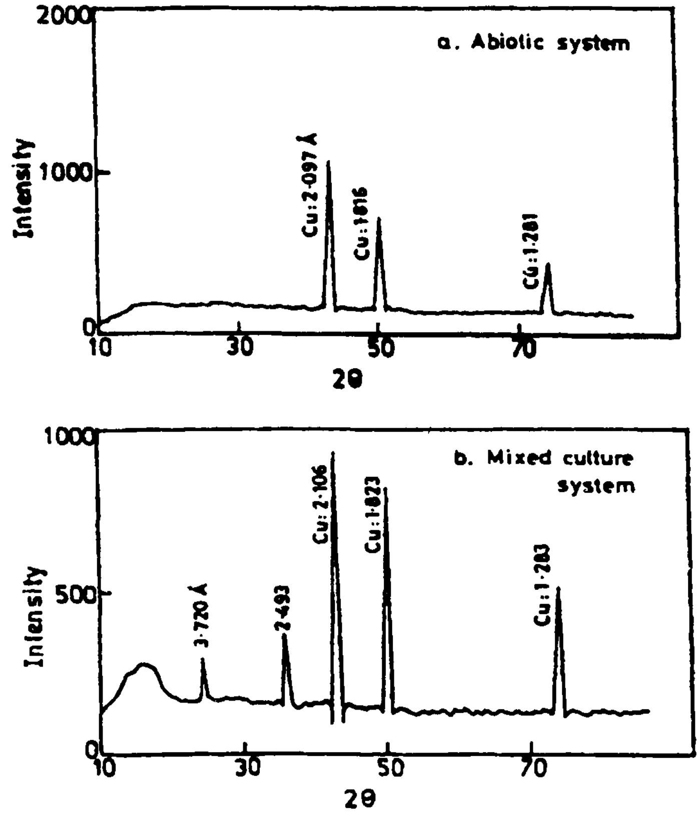

Fig. 6: XRD pattern of corrosion product of copper in mixed culture system and abiotic system.

CONCLUSION

Bacteriologically produced biofilm, which contains exopolymeric substance, reduces the corrosion of copper. Low corrosion rates were observed by weight loss method, polarization studies and impedance technique in bacteriologically produced biofilm systems. From the XRD analysis, in addition to the copper peaks, broad organic peaks were obtained for corrosion products formed on copper exposed to natural pond water and in a mixed culture system.

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