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Corrosion of Copper in Polluted Sea Water

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The corrosion potential and corrosion rate of electrolytic touch pitch copper in sea water containing hydrogen sulphide were investigated. Metal subjected to the action of sulphide was subsequently exposed to the harbour waters. The results indicated that in the putrid media corrosion rate of copper was low in the presence of high levels of sulphide and low levels of oxygen. These studies have also shown higher rate of corrosion on subsequent exposure to flowing sea water containing sulphide and dissolved oxygen.

Key words : Copper, corrosion, sulphide pollution.

Corrosion behaviour of ocean engineering metals and alloys in polluted waters of harbour and estuaries has gained importance in the light of the rapid growth in offshore activities. Corrosive nature of polluted water on fitting out basins was observed by Gudas *et al.* (1976). Rowlands (1965) showed that when there was sulphide pollution, failure of copper-nickel alloys occurred within a pH range of 7.5 to 5.5. The protective film formation on metals by clean sea water and corrosive nature of polluted water on this protective film were reported by Gillbert (1954). The effects of sulphide (Akolzin & Bogachev, 1969), mercaptans (Wall & Davies, 1965) and cystine (Tanabe, 1964, 1965) on copper based alloys have been studied. Mor and Beccaria (1975) studied the effects of pH on corrosion of copper in sea water containing sulphides and concluded that presence of sulphide increased the corrosion rate when the pH was above 7.2. The adverse effect of hydrogen sulphide in aerated sea water on the corrosion resistance of copper alloys have been investigated by Gudas *et al.* (1976) and Schulter (1978). Several studies on the susceptibility of copper alloys to sulphide contamination (Syrett *et al.*, 1979; Macdonald *et al.*, 1978, 1979; Gudas and Huck, 1979) have helped to identify the effects of concentration of sulphide, duration of exposure and pH on the corrosion rate.

Though copper-nickel alloys are the first choice for several marine installations, copper and brass still continue to be in use. There are no references available on corrosion of these in polluted tropical waters. An attempt was therefore made to study the effect of sulphide on copper in tropical harbour waters.

Materials and Methods

The metal under investigation was electrolytic touch pitch copper. Strip coupons, measuring 50 x 25 x 1.6 mm as per ASTM (1974) (Designation G 31-72), were used for general corrosion test. The panels were cleaned by electrolytic method as described in ASTM (1974) (Designation G I-72). The specimens were washed well with water and then with methanol, dried in air, kept for 24 h in a desiccator and weighed to an accuracy of ±0.1 mg. Four specimens were used for each test.

Surface sea water was collected one day prior to the start of the experiment from a place off Cochin, where water depth was approximately 100 metres. The samples collected recorded a salinity of 35.2‰ and a pH of 8.4. As the ratio of volume of solution to area of specimen was to be kept at 20 ml cm^{-2} (Efird & Lee, 1979), 100 ml sea water was taken in 1 litre glass beaker for immersion of two panels. A supporting plastic device was used to hold the panels upright. After positioning the panels in the beaker, the test medium was introduced. The small air column above the solution was replaced by nitrogen and the beaker was sealed air tight by using aluminium foil (polypropylene film coated surface facing the solution) and adhesive tape. The experimental cells were kept at 30±1°C. Effects of hydrogen sulphide on the metal was tested in natural sea water to which vegetable matter (salvania) and animal tissue (oyster meat) were added to produce hydrogen sulphide. The environmental details to which strip coupons were exposed are given in Table 1.

During the course of the experiment the chemistry of the media, the corrosion rate and the changes in electrode potential of metals were determined up to 25 days. Dissolved sulphide was determined by using p. phenylenediamine method, dissolved oxygen by modified Winkler method and ammonia by pyrazolone method (Strickland & Parsons, 1968). pH was monitored using a digital pH meter. The potential of the metal was measured using micro volt meter (Philips GM 6020). After 25 days, the panels were taken out from the medium, washed in water and cleaned electrolytically (ASTM, 1974; Designation GI-72). The corrosion rate was determined after applying the blank correction (Ailor, 1971).

After completion of the tests for a duration of 25 days, a set of four specimens were removed from the putrid sea water. They were then exposed to natural sea water at the Test Station (Fig. 1) for a further period of 25 days and the potential and rate of corrosion were determined.

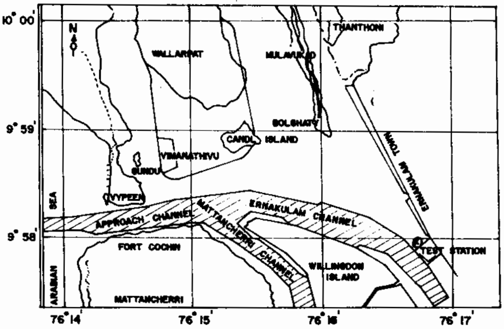

Fig. 1. Cochin Harbour showing the test station

The data were processed statistically by regression analysis (Snedecor & Cochran, 1968) to examine the relationship between the corrosion rate, sulphide concentration, pH and number of days of exposure.

Results and Discussion

The corrosion rates and variations of corrosion potential of metal exposed to sea water in the presence of sulphide

Table 1. Composition of putrid sea water media

Cell	Metal	Designation	Composition
1	Copper (ETP)	Control	1000 ml sea water
2	Copper (ETP)	5% plant	950 ml sea water + 50 g salvania
3	Copper (ETP)	5% meat	950 ml sea water + 50 g oyster meat
4	Copper (ETP)	2.5% plant + 2.5% meat	950 ml sea water + 25 g salvania + 25 g oyster meat

Table 2. Potential and corrosion rate of metal panels exposed to putrid sea water and natural sea water

Cell	Exposure, (days)	Potential mV (SCE)	Corrosion rate, µg year-1	Sulphide mg l^{-1}	Dissolved oxygen ml l^{-1}	pH	NH3 mg l^{-1}	Nature of panels after test (visual observations)
Cu (ETP) Sea water (Control)	0	-200	-	0.0	7.2	8.23	0.17	Bright
	25	-250	34.61	0.0	5.4	7.95	0.01	Tarnished, underlying metal slightly visible
	25 days in control + 25 days in natural sea water	-180	85.68	0.0	7.5	8.30	0.0	Bright with islands of green patina
Cu (ETP) plant, sea water	0	-215	-	0.0	5.0	7.46	0.77	Bright
	25	-430	1.57	88.6	0.0	7.00	0.05	Patches of shiny adherent black corrosion products
	25 days in putrid sea water + 25 days in natural sea water	-190	34.19	0.0	7.5	8.30	0.0	Slightly tarnished with islands of green patina
Cu (ETP), meat, sea water	0	-220	-	0.0	5.0	6.91	0.12	Bright
	25	-800	12.10	240.2	0.0	7.00	0.40	Adherent shiny black corrosion film
	25 days in putrid sea water + 25 days in natural sea water	-200	87.1	0.0	7.5	8.30	0.0	Slightly dull with islands of green patina
Cu (ETP) plant, meat, sea water	0	-220	-	0.0	5.2	7.13	0.15	Bright
	25	-800	12.24	149.0	0.0	6.93	0.24	Adherent black film
	25 days in putrid sea water + 25 days in natural sea water	-210	89.09	0.0	7.5	8.30	0.00	Patches of green patina

are given in Table 2. Data on corrosion of the above metal exposed to natural sea water for 25 days during the second phase of the experiment are also given in Table 2. The simple correlation coefficients between pairs of variables and the multiple regression equations are presented in Table 3.

Tests showed an appreciable change in the characteristics of the test solution and appearance of the metal from the second day of the experiment. During the course of the experiments, pH, concentration of sulphide and ammonia of the test solutions showed appreciable increase compared to the control. Rise in sulphide concentration was faster in the medium containing animal tissue. It may be seen from Table 2 that the shift in pH was associated with the anoxic condition that existed in the test media. In the absence of oxygen, the sulphate reducing bacteria act upon organic matter. The putrefaction leads to a sequence of events, mainly the depletion of oxygen, followed by denitrification, sulphate

Table 3. Mean, standard deviation, correlation coefficient between pairs of factors and R^2

		X_1	X_2	X_3	X_4	rX_1X_2	rX_1X_3	rX_1X_4	rX_2X_3	rX_2X_4	rX_3X_4	R^2
1	Mean		7.97	12.833	35.497				0.1524	0.12233	0.03396	0.1463
	S.D.		0.10392	8.8412	2.1396							

X_1 Sulphide (mgl^{-1})
X_2 pH
X_3 Period of immersion
X_4 Corrosion rate
R^2 Amount of variability explained by the regression

reduction and finally results in the formation of sulphide (Richards, 1965).

Examination of the analytical results showed that the extent of corrosion was significant after 5 days of exposure of the metal to the putrid medium. It is to be noted that by this time oxygen was reduced to the minimum. There was an increase in the level of sulphide and a slight increase in pH. None of the putrid solutions showed a pH of more than 7.5.

A comparison of the corrosion data pertaining to the period of significant build up of sulphide showed that the corrosion rate did not depend on the concentration of hydrogen sulphide, within the levels tested. The extent of corrosion in this case was significantly less than that of the metal exposed to sea water containing air. The dependence of corrosion on dissolved oxygen was clear from Table 2. When the dissolved oxygen was reduced to very low levels the corrosion rate decreased significantly in spite of increased levels of sulphide.

The data on the corrosion behaviour of pure copper in putrid sea water or water containing H_2S under tropical conditions are not available in literature. Most of the results available pertain to copper-nickel alloys only. Syrett (1977) suggested that in the absence of oxygen, the presence of hydrogen sulphide ensures reducing conditions which account for reduced corrosion rate. Copper probably suffers some attack from the reaction $2Cu+H_2S \longrightarrow Cu_2S+H_2$ or some equivalent reaction to which HS^- ions are the reactive species. In the presence of traces of oxygen, the reaction products are Cu_2S and H_2O.

Earlier studies (Syrett, 1977) in flowing water contaminated with sulphide have shown that Cu_2O_2, Cu_2S and CuS will tend to form on a competitive basis depending upon the oxygen-sulphide ratio. Owing to differences in the crystal structures, the growth of one crystal may impinge on a neighbouring crystal, leading to structural defects. This will lead to high corrosion rate by allowing the corrodent relatively easy access to metal surface. The presence of highly adherent Cu_2S might be contributing to an impervious film which resist continued corrosion of the metal. The above facts explain the observed low corrosion rate of copper in the absence of oxygen and in the presence of high level of sulphide. The work of Giuliani & Bombara (1973) supports this view.

Immediately on exposure to the putrid media the corrosion potential of copper was active by 15 to 20 millivolt and the potential shift was significant during the subsequent period also. This was particularly evident in the medium in which the sulphide generation was higher. The change in the water chemistry has caused a shift in potential by approximately 525 millivolt in 10 days. The transition from the thin film of oxide found on the metal to sulphide film on exposure to polluted sea water was accompanied by a shift in potential (Gudas *et al.,* 1976).

Exposure of the sulphide-treated metal to fresh flowing natural sea water at Test Station in the Cochin Harbour has resulted in dramatic changes in the corrosion rate, corrosion potential and surface corrosion film. The corrosion rate increased up to 20 times. The increased corrosion rate generally was due to the potential transition of the pre-exposed metal on exposure to unpolluted sea water. Similar observations were made by Gudas *et al.,* (1976) and Syrett (1981) for copper-nickel alloys. This potential shift runs parallel to the formation of the surface film on the metal. The surface of specimens that were exposed to putrid media were covered by adherent black lustrous film which gradually changed to dull black and finally to islands of green patina in 25 days.

The transformation of Cu_2S to Cu_2O on 90:10 cupro nickel involves a volume change from 28.4 to 23.9 cm^3mol^{-1} which weakens the bond between the black scale and oxide-type sub scale or between neighbouring particles within the thick scale (Syrett, 1981). This favours conditions leading to spalling of the sulphide layer in patches which might induce galvanic corrosion. Therefore, the high rate of corrosion of the sample exposed to hydrogen sulphide can be viewed as due to the conjoint action of loosing the sulphide layer, potential difference between the sulphide film and the spalled off areas and by hydrodynamic action of natural environment. Another factor which Syrett (1981) has attributed to the increased corrosion of 90:10 cupro nickel in aerated unpolluted sea water after exposure to sulphide polluted de-aerated sea water was the presence of poly sulphide and other oxidation products of sulphide within the pores of the black scale or in dead spaces within the flow system.

Regression analysis showed that rates of corrosion were found to decrease with increase in number of days as shown by significant negative correlation. Significant correlation was observed between sulphide concentration and number of days through out the experimental period. Significant negative correlation was observed between sulphide and corrosion rate in general.

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