

Effect of Sulphide on Admiralty Brass in Seawater

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The corrosion behaviour of admiralty brass in putrified seawater has been studied. It was observed that when the dissolved oxygen in the putrified seawater medium has attained very low value (< 0.53 p.p.m) the corrosion rate of admiralty brass showed decreasing trend inspite of increased level of sulphide from 21.2 to 228 p.p.m. Significant correlations (negative) were observed between corrosion rates and log period of exposure.

The corrosion behaviour of copper and its alloys in natural seawater has been studied in detail and well documented. The nature of accelerated corrosion of cupronickel piping in naval ships was studied in detail by Niederberger *et al.* (1976). This study has generated considerable interest on the sulphide induced accelerated corrosion of materials in seawater. The performance of copper and its alloys when exposed to attack by polluted seawater encountered in many harbours, are not well understood. The adverse effect of dissolved sulphide on the corrosion of copper-base alloys has been reported by several investigators (Rowlands, 1965; Akolzin & Bogachev, 1969; Mor & Beccaria, 1974, 1975; Bates & Popplewell, 1975; Macdonald *et al.*, 1979; Efrid & Lee, 1979). Fink & Boyd (1970) reported that in polluted seawater aluminium brass suffered severe corrosion compared to 70/30 cupronickel whereas in clean water the performances of aluminium brass and 90/10 cupronickel are similar. Among the principle sources of sulphides in seawater, those due to the action of sulphate-reducing bacteria under oxygen free conditions, the natural sulphate content of the seawater and putrefaction of sanitary or industrial sewage are of importance. When hydrogen sulphide is present in the water, a non protective black film containing copper sulphide can form on the surface of previously unexposed alloys (Vreeland, 1976). This film is more noble (Gilbert, 1954, 1959) upto 50 mV (Kenworthy, 1965) than the film normally formed in fresh water and behave cathodically towards the underlying metal. If there are breaks in the sulphide film, local attack is stimulated greatly by the

large area of active cathode (Schumacher, 1979). Bates & Popplewell (1975) concluded that a corrosion product film of Cu_2O with small amount of Cu_2S appears to be highly defective and much less protective than one in which Cu_2S is absent. Sato (1970) has noted that sulphide ion content of 0.05 p.p.m. in seawater is active enough to cause severe corrosion. The susceptibility of copper-nickel alloys to accelerated corrosion in seawater, having low sulphide concentration, was studied by Gudas & Hack (1979). Pillai (1985) studied the behaviour of copper in laboratory prepared samples of putrified seawater and found that the absence of oxygen, in the polluted seawater, sulphide ions favoured a reduction in the corrosion rate. The mechanism of corrosion of copper nickel alloys in sulphide polluted seawater was studied by several workers (Macdonald *et al.*, 1978, 1979; Syrett *et al.*, 1979; Syrett & Wing, 1980). But there are no published reports on the corrosion of admiralty brass in putrid seawater. The present study was made in putrid seawater under controlled conditions, where several variables have been reduced.

Materials and Methods

The chemical composition of admiralty brass used in the investigation is given in Table 1. The panels of size 50 x 25 x 1.6 mm were cut as per ASTM designation G31-72 (ASTM standards 1974b) from rolled sheets of 2.4 x 0.9 m and were used in the tests. The panels were cleaned by electrolytic method as described in ASTM designation G1-72 (ASTM standards 1974a) and washed well

Table 1. *Properties of metal used*

Metal used	Nearest specification	Sp. gravity	Elements determined	% elements
Admiralty brass	Inhibited admiralty CDA 443	8.53	Copper	69.42
			Zinc	28.41
			Tin	2.10
			Lead	0.35
			Iron	0.06
			Others	remainder

Table 2. *Composition of the test solutions*

Cell	Metal	Designation	Composition
1	Admiralty brass	Control	1000 ml-seawater
2	Admiralty brass	5% plant	50 g-salvania 950 ml-seawater
3	Admiralty brass	5% meat	50 g-oyster meat 950 ml-seawater
4	Admiralty brass	2.5% plant + 2.5% meat	25 g-salvania 25 g-oyster meat 950 ml-seawater

with water, followed by methanol. They were dried well in air and weighed. Four specimens were used in each test. The test solution was natural surface seawater collected one day earlier at a place off Cochin where the water depth was approximately 100 meters. The salinity and pH of the seawater were 35.2‰ and 8.4 respectively. To maintain a ratio of volume of solution to area of specimen at 20 ml cm⁻², 1000 ml of seawater was taken in one litre glass beaker for immersion of 2 panels. To keep the panel in upright position, a supporting plastic device was used. The small air column above the test medium was replaced by nitrogen and the beaker was sealed airtight by using aluminium foil and adhesive tape. The details of the medium are given in Table 2. The corrosion rate of panels and sulphide concentration in the medium were measured at intervals of 2, 5, 10, 15, 20 and 25 days. Dissolved sulphide was determined by using p. phenylenediamine method, dissolved oxygen by modified Winkler method as recommended by Strickland & Parson (1968). At the termination of the experiment, the

panels were taken out from the medium, washed well and nature of the metal surface observed. On cleaning electrolytically (ASTM standard 1974 a) the corrosion rate was computed after applying the blank correction.

Results and Discussion

The experimentally determined corrosion rates of the admiralty brass exposed to putrid seawater for different duration and concentrations of sulphide during the tenure of the experiment and summary of observations of the surface of metals after each test are given in Table 3. From the second day onwards of the test, the metal surfaces showed varied appearances ranging from bright through dull to a lustrous black colour. Control panels changed from bright to dull on the second day and no further change was noticed thereafter. The sulphide concentration registered a rapid increase evidencing putrefaction reactions occurring in the media. The sulphide content showed steep rise in animal putrified medium than

Table 3. *Results of the exposure of admiralty brass in the putrid seawater*

Cell	Period of exposure days	Sulphide expressed as S ⁻ mg l ⁻¹	Corrosion rate $\mu\text{m yr}^{-1}$	Nature of panel after test (visual)
1 (Control)	0	0	0	Bright
	2	0	74.68	Slightly tarnished, underlying metal visible
	5	0	25.26	Tarnished, underlying metal slightly visible
	10	0	14.16	Tarnished, underlying metal slightly visible
	15	0	14.01	"
	20	0	12.83	"
	25	0	9.86	"
				"
2 (Plant + seawater)	0	0	0	Bright
	2	21.2	56.32	Tarnished, partially underlying metal visible
	5	30.0	17.17	Tarnished, patches of black deposits
	10	48.0	11.61	Shiny black adherent coating
	15	54.0	8.47	"
	20	60.1	6.49	"
	25	79.2	6.49	"
				"
3 (Meat + seawater)	0	0	0	Bright
	2	108.0	21.5	Tarnished, partially underlying metal visible
	5	168.0	13.58	Tarnished, underlying metal slightly visible
	10	209.0	2.69	Shiny, black adherent coating
	15	220.0	2.39	"
	20	235.0	1.75	"
	25	228.0	1.19	"
				"
4 (Meat + plant + seawater)	0	0	14.01	Bright
	2	81.6	14.01	Slightly tarnished underlying metal visible
	5	96.5	8.64	Tarnished, underlying metal slightly visible
	10	108.2	4.27	Tarnished, patches of black shiny coating
	15	130.4	3.58	Adherent shiny black coating
	20	135.2	2.22	"
	25	138.8	1.47	"
				"

Table 4. *Correlation matrix*

	Cell No.	Log period of exposure	Hydrogen sulphide content
Corrosion rates	1	-0.90*	-
	2	-0.91*	-0.77
	3	-0.96**	-0.98**
	4	-0.94**	-0.94**
Log period of exposure	1	-	-
	2		0.95**
	3		0.98**
	4		0.98**

in the set up that contained plants. Analytical results show that the oxygen depletion progresses from the 2nd day and after 5 days the oxygen content is reduced to zero. In the absence of oxygen, the sulphate reducing bacteria act upon the organic matter. The putrifaction sets in a sequence of events, mainly the depletion of oxygen followed by denitrification, sulphate reduction and finally results in the formation of sulphide (Richards, 1965). In the putrified media, the presence of *Desulfovibrio* spp. was detected using Starkey's medium by the method described by Skerman (1959). A perusal of results in Table 3 shows that when the dissolved oxygen has attained very low value, the corrosion rate showed a decreasing trend inspite of increased level of sulphide. The metal suffers some attack by the reaction with hydrogen sulphide forming sulphide or hydrogen or equivalent reaction to which HS⁻ ions are the reactive species. Several factors may be expected to contribute to the decreased corrosion rate. In the highly oxygen depleted medium Syrett (1977) has pointed out that the presence of hydrogen sulphide ensures reducing conditions which might account for reduced corrosion rate. Yet another factor is the formation of sulphides of the metal which form on impervious layer shielding the metal from the reactants. The works of Giuliani & Bombara (1973) suggested this. Syrett (1977) has also reported that the presence of either (1) sulphide (48 to 1940 ppb) plus low oxygen (29 to 60 ppb) or (2) oxygen alone (865 to 6950 ppb) lends to low corrosion rates. When both sulphide and oxygen are present in certain concentrations, dramatic increases in the corrosion rate result. The present

study has shown that the increase in corrosion rate is very small with increase of sulphide concentration 21.2 to 228 p.p.m. when the oxygen concentration falls below 0.53 p.p.m.

Correlation coefficients between corrosion rates and logarithm of period of exposures, corrosion rates and hydrogen sulphide content and also logarithm of period of exposures and hydrogen sulphide content were worked out. Significant correlations (negative) were observed between corrosion rates and long period of exposure (Table 4). Correlation coefficient (negative) between corrosion rates and hydrogen sulphide content were found to be significant for the cell numbers 3 & 4. For cells 2 to 4, highly significant (positive) correlations between period of exposure (log) and hydrogen sulphide content were observed. As the period of exposure (log) and hydrogen sulphide content are highly correlated (positively) corrosion rate is found to be related to either the days of exposure (log) or the hydrogen sulphide content.

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