

Corrosion behaviour of metals and alloys the waters of the Arabian Sea

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FOUR TYPES of metals (mild steel, brass, aluminium and stainless steel) were exposed during the period November, 1987, to November, 1988, at depths exceeding 1000m in the Arabian Sea, in order to assess their behaviour with respect to corrosion. The results indicated an increase of the corrosion rate of mild steel and brass with increased depth, whereas in the case of stainless steel and aluminium, the corrosion rate decreased with increased depth. This difference in behaviour with respect to depth could be attributed to the characteristic way that metals and alloys react with the dissolved oxygen present in the water column.

Introduction

Increased maritime activities due to the exploration and exploitation of marine resources have urged the need to assess the behaviour of metals and their alloys in a wide range of marine environments. These environments include estuarine, near-shore, off-shore and the deep sea. As far as Indian waters are concerned, very little work has been reported in regard to the corrosion of various metals and alloys in these environments[1-7]. To date, no report is available on the corrosion behaviour of metals in deep waters along the Indian coast. In order to fill this gap of knowledge, the present investigations were undertaken.

Four types of metals, including commercial-grade mild steel, brass, aluminium and stainless steel, were selected for deep-water exposure. The metallic coupons were exposed at two different depths ranging from 1000-2900m at three different locations in the Arabian Sea. The studies were carried out from November 1987 to November 1988.

Experimental method

Panels sized 10x6cm were cut from sheets of commercial-grade mild steel (C 0.20%, Si 0.05%, Mn 0.26%, P 0.052%, S 0.04%, Fe the rest), brass (Zn 32.55%, Cu the rest), aluminium (Si 0.15%, Mn 0.8%, Al the rest) and stainless steel (C 0.06%, Si 0.009%, Mn 1.0%, Cr 14%, Ni 7.09%, Fe the rest). The panels were initially cleaned and weighed as recommended[8]. The unprotected panels were mounted on the hexagonal cages of mild steel, with double insulation provided with the help of pvc nuts, bolts and washers. These cages were maintained at two different depths with the help of a deep-sea mooring system used for sediment traps. The depths under study were 1000m and 2400m at a station in the Western Arabian Sea (WAST, 16°23'N, 60°29'E); 1400m and 2900m in the Central Arabian Sea (CAST, 14°35'N, 64°50'E); and 1300m

and 2800m in the Eastern Arabian Sea (EAST, 15°15'N, 68°35'E) (Fig.1). In order to have as wide a coverage of exposure as possible, the panels were exposed at depths ranging from 1000-2900m.

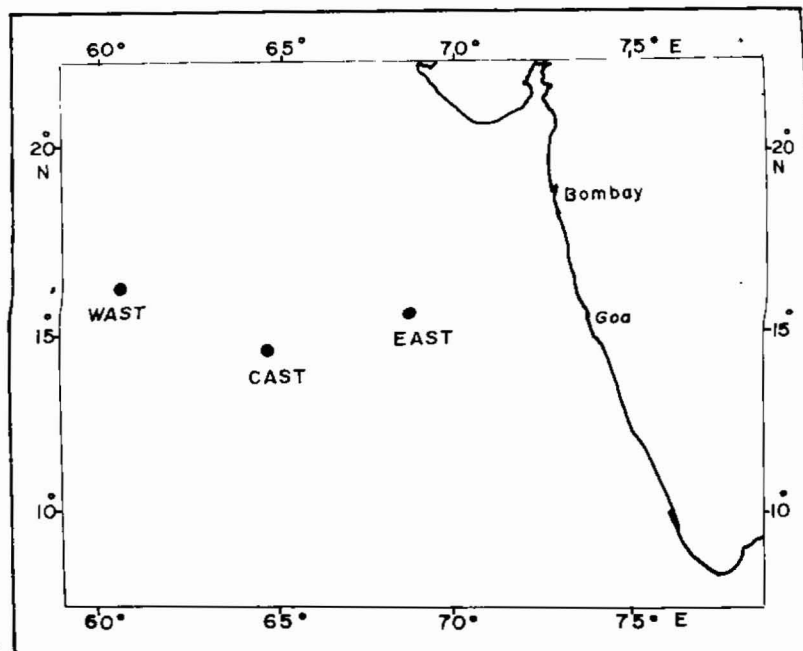
Immediately after retrieval, the panels were photographed and cleaned, following standard procedures[8]. The panels of mild steel, brass and aluminium were cleaned for corrosion product as recommended[8]. The stainless steel panels were gently brushed with a sponge, and rinsed with distilled water to get rid of the (micro) biofilm and salt. The cleaned panels were weighed after 24hrs of drying in a desiccator. The corrosion rates of mild steel, brass and aluminium have been expressed in terms of milligrams weight-loss per square decimeter area per day (mdd), whereas, in the case of the stainless steel coupons, the amount of weight gained by the metal has been expressed as mg/dm²/year. In addition, the stainless steel and brass panels were also studied under a scanning electron microscope (SEM) for assessing pitting and intergranular corrosion respectively. The panels of all four types were studied in triplicate. The data on salinity and dissolved-oxygen have also been collected at 500m intervals below 500m depth during November, 1987 and November, 1988.

Experimental results and discussion

Mild steel

The corrosion suffered by MS was of a general type. Approximately 2-mm thick corrosion product was found deposited on the panels (Fig.2A). The corrosion rates varied from 2.14-14.48mdd. Depth-related changes in the corrosion rates were prominent (Fig.3). The corrosion rates at all three stations increased with increasing depth (Fig.4). The extent of corrosion varied quantitatively from station to station, being more at CAST and less at WAST; this difference has been attributed to the variations in the depths of exposure at different stations. The depth of exposure at the upper and

Fig.1. The location of mooring stations in the Eastern (EAST), Central (CAST) and Western (WAST) Arabian Sea.



lower levels was a maximum at CAST (1400m and 2900m) and a minimum at WAST (1000m and 2400m). The dissolved-oxygen concentration and salinity distribution profiles are shown in Fig.5. The dissolved-oxygen concentration increased with depth, whereas salinity decreased with increased depth. The data on corrosion indicated a close relationship with dissolved-oxygen concentration ($r=0.97$), and was negatively correlated with salinity ($r=-0.94$). These observations indicate that the higher dissolved-oxygen concentrations at greater depth may have a conducive effect on the corrosion process of mild steel.

Brass

The data indicate that the alloy suffered corrosion to a comparatively lesser extent than mild steel. However, the depth-related pattern was identical to that of mild steel (Fig.4). The increase in corrosion-rate at greater depth was approximately 30%. In this case also, the corrosion rates and the values of dissolved-oxygen concentration from the respective depths showed a very close relationship ($r=0.94$), whereas corrosion and salinity were negatively correlated ($r=-0.81$). The increase in corrosion rates was associated with increased dissolved-oxygen concentrations at greater depths, which suggests that a higher level of dissolved-oxygen concentrations at the greater depth might have enhanced the corrosion rates of brass. The surface morphology of the corroded



Fig.2A (right, top). Photograph of the mild steel panel from 2900m depth, showing the thick layer of corrosion product.

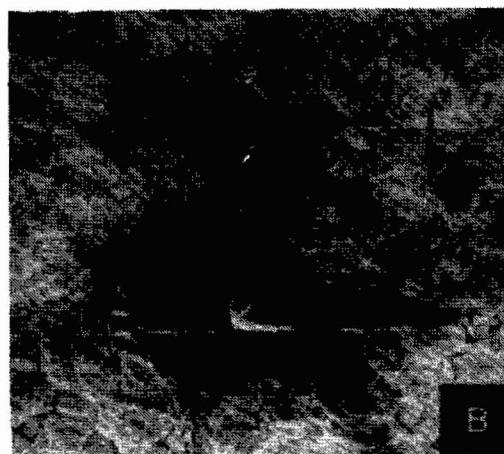


Fig.2B (right, bottom). SEM (x800) of the brass panel from 2900m depth, showing intergranular corrosion.

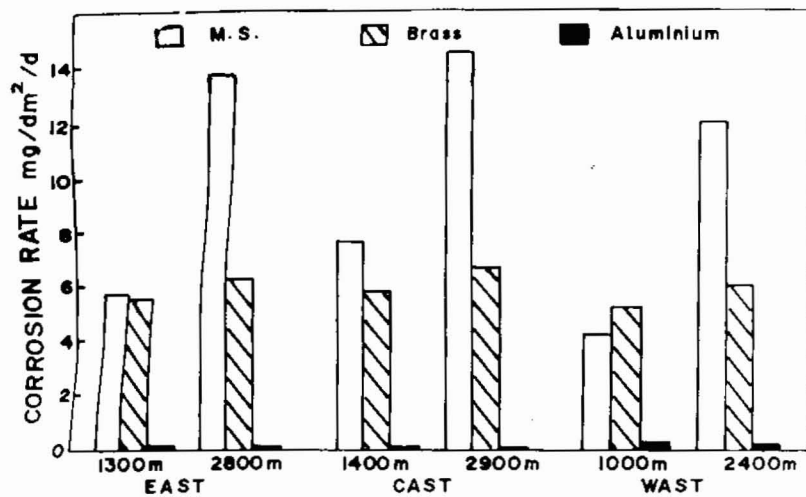


Fig.3. Rate of corrosion of mild steel, brass and aluminium exposed at different depths in the Arabian Sea.

alloy indicated intergranular attack, which is believed to be the characteristic nature of copper alloy for sea-water exposure (Fig.2B).

Aluminium

From Fig.3, it appears that the aluminium coupons suffered least loss due to corrosion, thereby proving the metal's high resistivity to deep-water exposures. The corrosion rates of this metal were comparatively less than those for mild steel and brass, varying from 0.1-0.2mdd. The loss of metal was assumed to be due to pitting at the edges, and otherwise no significant surface attack was observed. An interesting feature was observed in the behaviour of aluminium to deep-sea exposure. The corrosion rates decreased with increasing depth which was a common feature at all three stations (Fig.6). The decrease of corrosion rates

with increased dissolved-oxygen concentrations ($r=-0.9$) suggests the extent of passive hydrous oxide film formation, which might have offered protection to the metal from reacting with the surrounding environment[9].

Stainless steel

Apparently no surface attack was observed on the panels on visual examination. However, the results of SEM investigation revealed that the alloy was attacked by corrosion along the grain boundaries. Fig.7 shows the SEM micrographs of the panels exposed at different depths at all three stations. The results show inverse relation of the corrosion of the alloy with variations of dissolved-oxygen concentrations. The panels exposed at upper depths showed a greater number of micropits and, to some extent, widening of grain boundaries as compared with the panels exposed at deeper levels. This indicates that the alloy was affected severely with less dissolved-oxygen and more salinity. As against this, at greater depths it was protected probably due to a higher concentration of dissolved-oxygen and less salinity. These observations are also in agreement to some extent with the data on weight-gain of the alloy. The panels exposed at the upper depths showed less weight gain, compared with the greater weight gain at greater depth (Table 1). The data thus provides clear evidence of the formation of higher amounts of oxide film on the surface of panels as a result of higher concentrations of dissolved oxygen at deeper levels. This oxide film, which is believed to

Fig.4. Variation of corrosion rates of mild steel and brass as a function of depth.

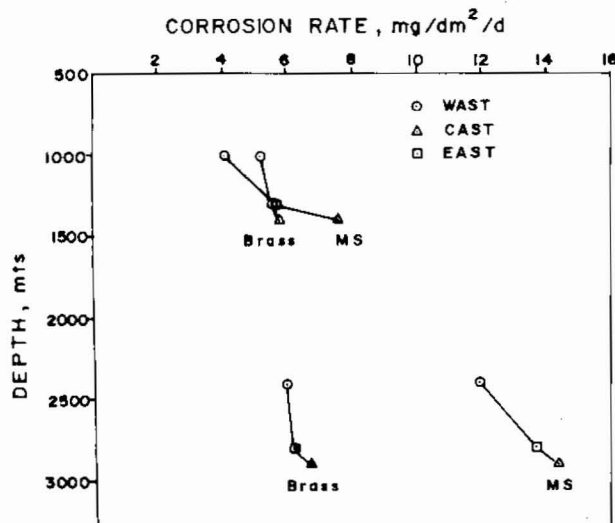


Table 1. Weight gain by stainless steel panels (mg/dm²/year).

Station	EAST		CAST		WAST	
Depth (m)	1300	2800	1400	2900	1000	2400
Values (mg)	5.93	7.41	6.66	8.17	5.73	6.64

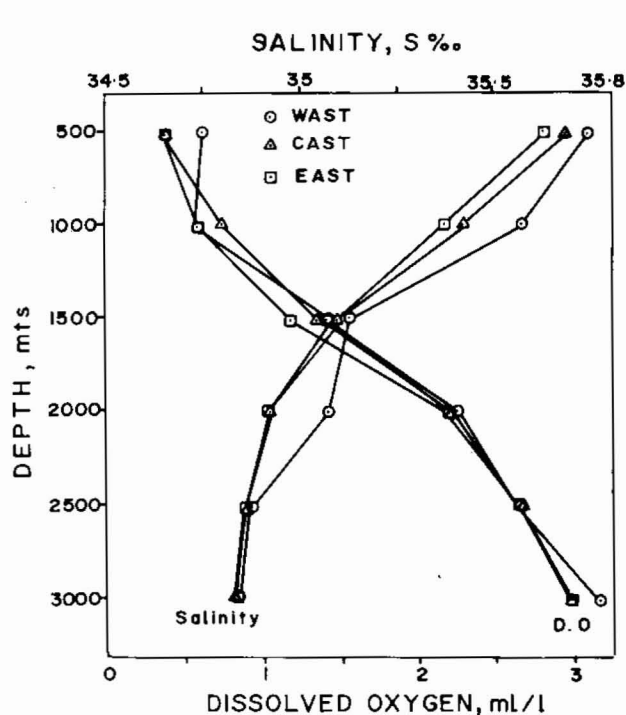


Fig. 5. Dissolved oxygen and salinity profiles at the three stations.

be very passive, might have provided protection to the alloy[10].

Overall view

From this investigation, it appears that the corrosion process at deeper levels in the water column is governed by dissolved-oxygen concentration rather than salinity. The higher

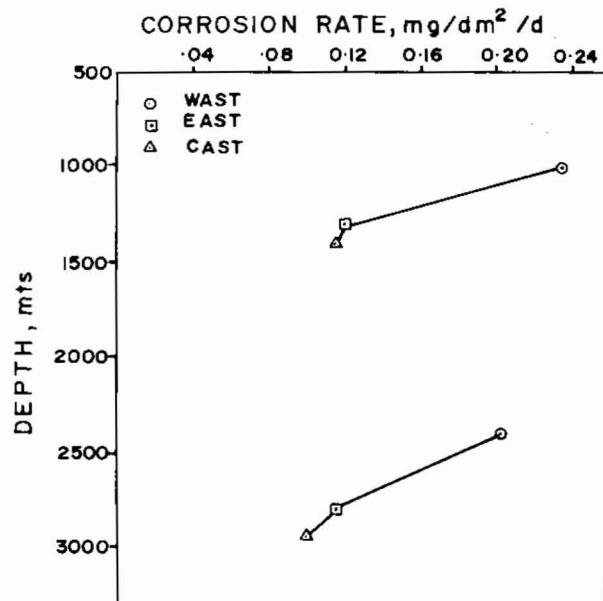
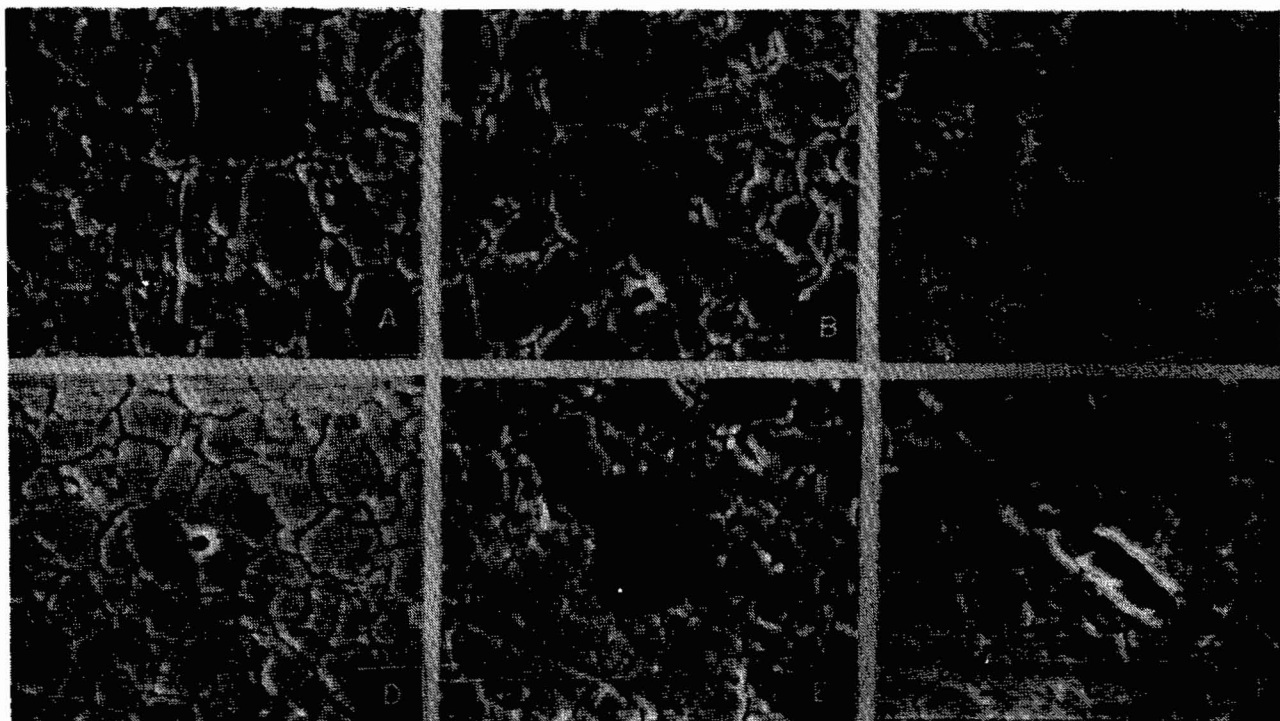


Fig. 6. The inverse relationship between the corrosion rates of aluminium with depth.

concentrations of dissolved oxygen at greater depth have caused more loss of mild steel and brass by serving as a cathodic depolarizer. However, the dissolved oxygen appears to have offered some degree of protection to aluminium and stainless steel by virtue of forming a higher amount of oxide film, which is very passive in nature. On the other hand, the low oxygen content at upper depth accounted for the much greater severity of corrosion of aluminium and stainless steel when

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Fig. 7. Scanning electron micrograph (x2000) of stainless steel panels, showing micropits and widening of grain boundaries. (A) 1000m and (D) 2400m, WAST; (B) 1400m and (E) 2900m, CAST; and (C) 1300m and (F) 2800m, EAST. (Note: Sample (F) shows an original artifact on the panel surface.)



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compared with high oxygen concentrations at greater depths. This is because the lower oxygen concentrations apparently reduce the protective effect of oxide film.

Secondly, the more saline waters at the upper levels might have caused more corrosion of aluminium and stainless steel. The possible role of water temperature in enhancement of corrosion of aluminium and stainless steel at the upper depths also cannot be ruled out. It is believed that the ability of chloride ions to penetrate and destroy passive film locally increases with temperature[10]. The observations made by Gopalkrishna[11] at the same sites in 1982 suggest that the temperature values at the upper depths (1000m) were 3-4 times higher than those at the lower depths (2900m). The combined effect of salinity and temperature probably explains the higher corrosion of stainless steel and aluminium at the upper depth and less at greater depth.

Conclusions

In general, the metals under study showed a varying degree of resistivity to deep-water corrosion. The resistivity towards the environment was in the increasing order of:

mild steel < brass < aluminium < stainless steel.

The corrosion rates of mild steel and brass increased with depth whereas, in the case of aluminium and stainless steel, the corrosion decreased with increasing depth. The higher concentrations of dissolved oxygen at the deeper levels was responsible for more loss of mild steel and brass, whereas it was responsible for providing higher degrees of protection to aluminium and stainless steel by virtue of forming higher amounts of passive oxide film on the surface.

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