

Corrosion of metals and alloys in the coastal and deep waters of the Arabian Sea and the Bay of Bengal

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Received 15 February 1993; accepted 4 August 1993

Corrosion rate of mild steel, stainless steel, copper, brass and cupro-nickel has been determined by exposing metallic coupons in coastal and oceanic waters of the Arabian Sea and Bay of Bengal. (Two stations each in the Bay of Bengal and the Arabian Sea were selected for deep water exposure, whereas, a single coastal station was selected in the Arabian Sea on the west coast of India.) Amongst the metals and alloys under study mild steel exhibited highest rate of corrosion. Stainless steel showed negligible corrosion rate in deep waters, whereas has been severely pitted due to macrofouling in coastal waters. In general the corrosion rates for all the metals and alloys under study are found to be higher for coastal waters than in deeper waters except, in case of brass. No significant difference in the corrosion rate of brass has been observed with respect to the depth. The observed order of corrosion rate is $MS > Cu > Cu-Ni > Br > SS$ in coastal waters and $MS > Cu-Ni > Br > Cu > SS$ in deep oceanic waters.

The ever increasing activities for exploration and exploitation of living and non-living resources from the sea has taxed the ingenuity of equipments, devices, structures and other marine facilities to be compatible with the hostile marine environments. The performance of any metals or their alloys could be assessed either in the laboratory or in the field. However, the materials tested in laboratory conditions may behave in unexpected manner in natural environment. This is because the natural marine environment is believed to be dynamic system which is governed mainly by physical, chemical and biological factors. Therefore, the data on the extent and nature of corrosion of metals and alloys exposed to natural sea-water will be more realistic and reliable than the data obtained by exposing the materials in laboratory simulated conditions.

Keeping in view of these points data on the corrosion rate for commercial grade mild steel, stainless steel, copper, cupro-nickel and brass have been determined from coastal and deep oceanic waters of Arabian sea and Bay of Bengal.

Experimental Procedure

Metallic coupons ($10 \times 8 \times 0.2$ cm) of mild steel (C-0.2%, Si-0.05%, Mn-0.26%, P-0.05%, S-0.04%, Fe-rest), stainless steel (S-0.009%, Mn-0.1%, C-0.06%, Cr-14%, Ni-7.09%, Fe-rest), copper (Ni-0.05%, Cu-rest), brass

(Zn-32.55%, Cu-rest) and cupro-nickel (Fe-0.8%, Ni-8.2%, Cu-rest) were cleaned following standard procedures¹ before immersion and weighed to constant weight. The cleaned coupons were exposed at five different locations in the Arabian sea and Bay of Bengal (Fig. 1). The coupons were mounted on fibre glass strips with PVC nut and bolts and suspended at two different depths at all the five locations. At coastal station ($16^{\circ}33'N$, $73^{\circ}20'E$) the depths of immersion were 0.5 m and 6 m below the water level, whereas, at oceanic stations (Arabian sea and Bay of Bengal) the depth of immersion ranged between 1000-2900 m. The coastal station was situated near the mouth of Vaghotan river and hence subjected to freshwater influx, during monsoon.

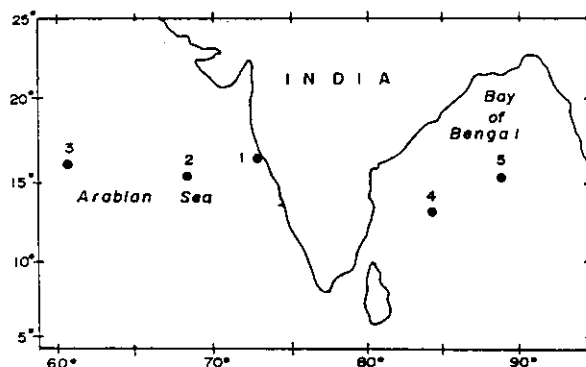


Fig. 1 - Sites location map

Four stations were selected in the oceanic waters. These stations were located at western Arabian sea (16°23'N, 60°29'E), eastern Arabian sea (15°15'N, 68°35'E), northern Bay of Bengal (15°14'N, 89°09'E) and central Bay of Bengal (13°08'N, 84°16'E). The coupons were exposed for 12 months (1989 to 1990) duration in submerged condition. At coastal station a raft was used for suspending the coupons whereas at oceanic stations deep sea mooring system was used (Fig. 2). After retrieval the coupons were examined for the extent and nature of macrofouling. The coupons were cleaned in cleaning solution for removal of the corrosion product as recommended¹. The corrosion rate was calculated by using the following formula and expressed as mils per year (mpy)².

$$\text{mpy} = \frac{534 W}{DAT}$$

where W = weight loss, mg

D = density of specimen, g/cm³

A = area of specimen, sq. inch

T = exposure time, h

In addition, some of the important physico-chemical parameters were also monitored.

Results and Discussion

The most distinct hydrological features at the coastal station were, temperature fluctuated between 21-28°C at 0.5 m and at 6 m the values varied between 20-27.5°C. Salinity ranged between 16.2-37.0 ppt. Dissolved oxygen ranged between 3.2-5.0 mL/L and 2.7-4.3 mL/L at 0.5 m and 6 m, respectively. Variations in the pH with respect to depth was not evident at coastal station. The pH ranged between 7.8-8.3 at both the depths.

At the oceanic sites the water temperature varied from 2.1°C at 2300 m to 6.4°C at 1000 m in Bay of Bengal, whereas, in Arabian sea it ranged between 1.6°C at 3000 m to 5.4°C at 1100 m. The salinity ranged between 34.84‰ at 3000 m to 35.37‰ at 1100 m. depth, whereas dissolved oxygen ranged between 0.56 mL/L at 1100 m to 3.18 mL/L at 3000 m in the Arabian sea. The values of salinity for the Bay of Bengal ranged between 34.76‰ at 2300 m to 34.93‰ at 1000 m whereas, the concentration of dissolved oxygen ranged between 1.0 mL/L at 1000 m to 2.9 mL/L at 2300 m. The pH ranged between 7.8 at 1100 m to 7.92 at 3000 m in Arabian sea, whereas, in

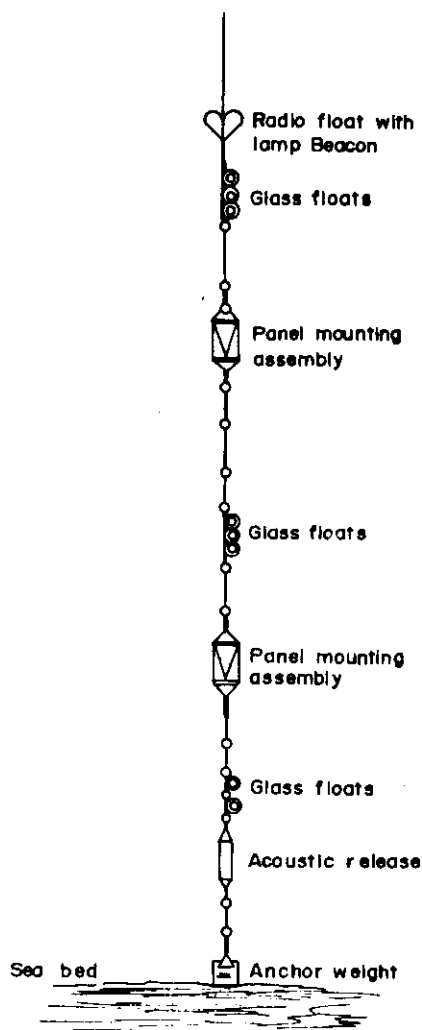


Fig. 2 - Schematic diagram of deep sea mooring system

Bay of Bengal the pH ranged from 7.68 and 7.72 at 1000 m and 2300 m depth, respectively.

Mild steel— Wide variation in the extent of corrosion of mild steel (MS) was observed with respect to the geographical location and depth of exposure. Mild steel coupons were densely fouled by barnacles at coastal station (biomass 1.8-2.3 kg/m²), whereas no fouling activity was observed on the coupons exposed to deep oceanic waters. At the coastal station the corrosion product was firmly adhered to the bare metal. The colour of the corrosion product was dark brown to black and produced H₂S with HCl which was a clear indication of the association of sulphide with the corrosion product. Contrary to this, the corrosion products for the deeper oceanic waters were soft and loosely held on to the surface of coupons and produced mild sulphide with HCl. The colour was brick brown to brown. The corrosion rates for

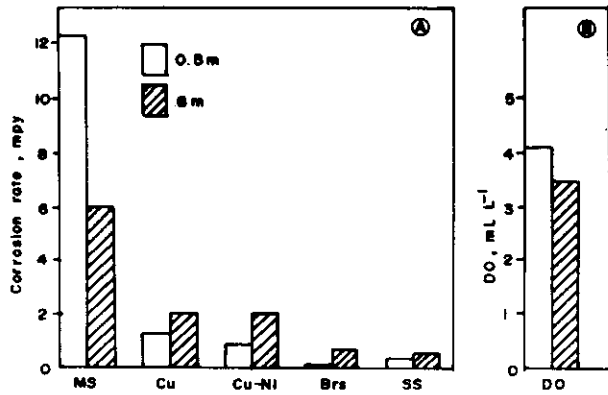


Fig. 3 - Corrosion rate of metals and alloys (A) and concentration of dissolved oxygen (B) in the coastal waters of the Arabian sea

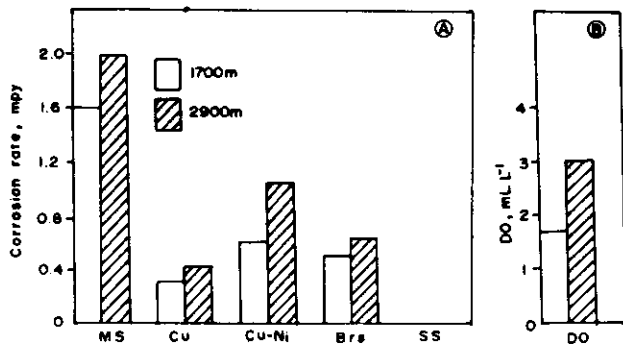


Fig. 4 - Corrosion rate of metals and alloys (A) and concentration of dissolved oxygen (B) in the deep oceanic waters of eastern Arabian sea

the coastal station varied from 5.9 to 12.2 mpy, whereas, for deep oceanic waters it was 0.8 to 2.3 mpy. Nearly 5-7 times increase in the corrosion rate was observed at the coastal station as compared to oceanic waters. The corrosion rate of MS decreased with increasing depth at coastal station, whereas, at oceanic sites the corrosion rate increased with increasing depth below 1000 m (Figs 3-7). Thus, it appears that hydrostatic pressure has no direct influence on the extent of corrosion of MS. However, dissolved oxygen concentration which varied greatly with respect to depth, might have influenced the rate of corrosion to a greater extent (correlation coefficient = 0.87). When the oxygen content and temperature vary together as they do in marine environment, the oxygen effect tends to predominate. This fact has been brought out from result obtained at depth. The corrosion rate decreases with dissolved oxygen down to oxygen minimum then increases again with oxygen at greater depth despite a continuing decrease in temperature. Therefore, the rate of corrosion is a function of dissolved oxygen

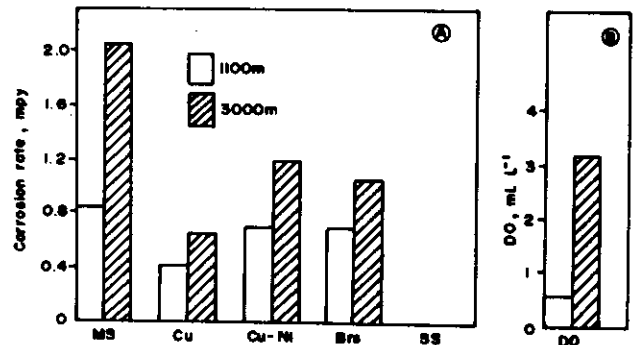


Fig. 5 - Corrosion rate of metals and alloys (A) and concentration of dissolved oxygen (B) in the deep oceanic waters of the western Arabian sea

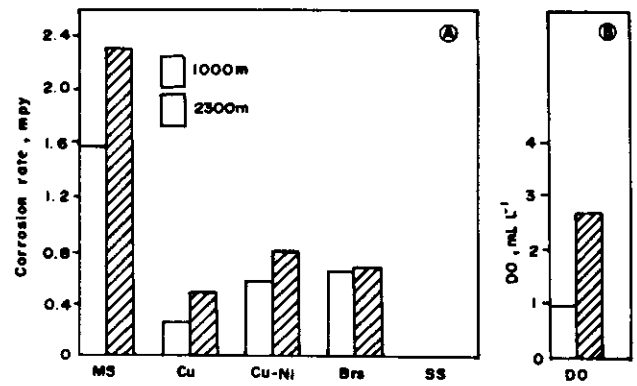


Fig. 6 - Corrosion rate of metals and alloys (A) and concentration of dissolved oxygen (B) in the deep oceanic waters of the central Bay of Bengal

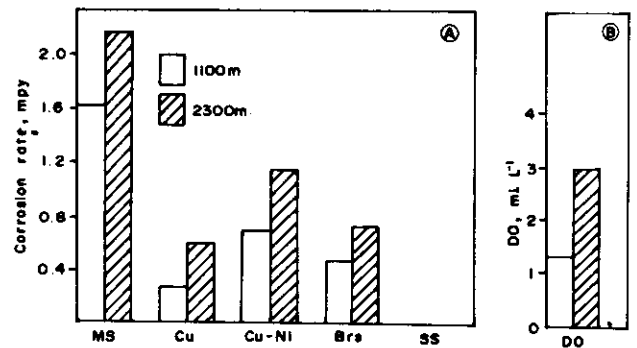


Fig. 7 - Corrosion rate of metals and alloys (A) and concentration of dissolved oxygen (B) in the deep oceanic waters of northern Bay of Bengal

content which is one of the major components of the cathodic reactant.

Stainless steel—Stainless steels usually undergo pitting and crevice corrosion in sea-water. Pitting is most likely to occur in presence of chloride ions combined with such depolarizer as oxygen. An oxidizing environment is usually necessary for preservation of passivity but unfortunately it is al-

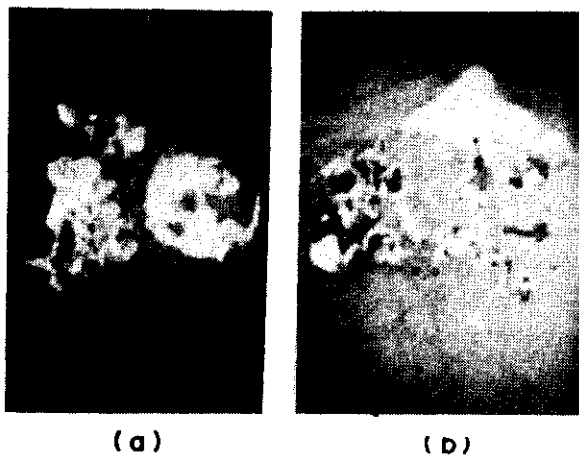


Fig. 8—Photomicrograph (10X) of the stainless steel par showing crevice and pitting corrosion under the base of dead barnacle shells

so favourable condition for pitting. The oxidizer can often act as a depolarizer for passive, active cells that were established by breakdown of passivity at specific area. The chloride ions in particular can accomplish this breakdown. According to the present observations the stainless steel under study was found to behave differently in coastal and deep oceanic waters. This alloy in coastal waters was severely perforated due to crevice and pitting type of corrosion especially under the base of calcareous shells of dead organisms (Fig. 8a & b). As regards to deep water, visibly no crevice/pitting was observed on stainless steel surface which could be due to the lack of macrofouling activities in deeper waters. Stainless steel possesses resistance towards corrosion mainly due to the presence of chromium which offers protection to the metal by formation of its passive oxide film. However, non-uniformity of the oxide film occurs due to the settlement of marine organisms causing different aeration cells. Under such circumstances the metal suffers crevice corrosion under the base of calcareous growth⁶.

The difference in behaviour of the alloy in these two environments is attributed to the intense macrofouling activities at coastal station (biomass, 2.2-3.4 kg/m²), which has resulted in the formation of crevices and pitting of the metal. Pitting and crevice corrosion are believed to be the most commonly encountered forms of attack in stainless steel particularly in marine conditions or under marine fouling³. Under-deposit corrosion is extremely important for alloys because it initiates a series of events that are individually or collectively extremely corrosive⁴. Dead barnacles, corrosion product debris or microbiological co-

lonies accumulating on the surface result in the formation of differential aeration cells⁵. The area immediately under the deposit becomes deprived of oxygen. That area becomes a relatively small anode compared to the large surrounding oxygenated cathode.

In deeper water fouling activity was not observed hence the passive oxide film might have remained intact. It is also believed that the ability of chloride ions to penetrate and destroy passive film locally increases with temperature⁵. The second reason for no pitting/crevice corrosion of stainless steel in deeper water could be due to the inability of chloride ions to attack the passive film owing to lower temperature prevailing at those depths (1.6-6.4°C).

Copper and its alloys—Among the metals under study no significant difference in the extent of corrosion of brass (Brs) was observed at all the five stations (Figs 3-7). The corrosion rate at all the five sites varied from 0.12-1.06 mpy irrespective of geographical location. This indicates that no site specific effect was observed on brass.

As regards to copper (Cu) and cupro-nickel (Cu-Ni), the corrosion rates were slightly higher for coastal station as compared to deep oceanic water. The corrosion rates for copper and cupro-nickel at coastal station varied from 1.36-2.08 mpy and 0.96-2.0 mpy, respectively. These values are in agreement with the data from Pacific water⁶. For oceanic water the rates ranged from 0.27-0.65 mpy for copper and 0.56-1.20 mpy for cupro-nickel. The coupons from all the locations were free from any macrofoulers. Dark green coloured corrosion product was found firmly adhered to the surface of the coupons which were exposed to the coastal station. The corrosion rate for copper and its alloys under study were found to increase with increasing depth irrespective of the site, probably due to the formation of non protective film in the absence of light⁶ (Figs 3-7). Similar results were also found in the Black sea⁶. Though, the depth related pattern was same for all the sites, the corrosion rates for copper and its alloys were higher at coastal site than deep oceanic water.

The higher rate of corrosion of copper and its alloys in coastal water is attributed to the higher concentration of dissolved oxygen and temperature at the site. Secondly, in coastal water erosion corrosion is more pronounced which is caused by the removal or break down of the protective film by mechanical forces such as local turbulence or impingement⁷. Differential aeration⁸, selective

leaching⁹, under-deposit corrosion and cathodic depolarization¹⁰ have been reported as mechanisms for microbiologically influenced corrosion of copper alloys. The components such as CO₂, H₂S, NH₃, organic and inorganic acids, metabolites and sulphur compounds – mercaptans, sulphides & disulphides – present in the sea water as a result of higher biological activities in coastal water may also accelerate localized attack in coastal water¹¹.

From the present observations it can be concluded that the metals and alloys behave differently in different marine environments. Metals and alloys corrode faster in coastal water than in deep oceanic water. In deep oceanic water concentration of dissolved oxygen influence the rate of corrosion of different metals and alloys whereas, in coastal water in addition to dissolved oxygen some other factors such as velocity, temperature, salinity and biofouling influences the corrosion of these metals and alloys. Stainless steel appear to be more susceptible for crevice and pitting corrosion in coastal water than in deep oceanic water.

Based on the performance of these metals and alloys in marine environments they can be arranged in the decreasing order of corrosion as MS > Cu > Cu-Ni > Brs > SS in coastal water, whereas, in deep oceanic water they were in the decreasing order of corrosion as MS > Cu - Ni > Brs > Cu > SS.

Acknowledgements

The authors are grateful to Dr B N Desai, Director, National Institute of Oceanography, Goa for his constant encouragements. Thanks are due to Mr R R Nair, Project Co-ordinator, INDO-FRG Project and Dr V Ittekkot of Geologisch – Palaontologisches Institute, Universitat Hamburg, FRG for providing necessary mooring facilities. Sincere thanks are also due to Mrs A Garg for the help in analyses of samples.

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