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Cathodic protection of mild steel and copper in deep waters of the Arabian Sea and Bay of Bengal

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Performance of cathodic protection system to mild steel and copper in deep (> 1000 m) oceanic waters of the Arabian Sea and Bay of Bengal has been assessed using aluminium and mild steel sacrificial anodes. The corrosion rates of unprotected metals as well as their percentage protection increased with increasing depth. The ranges of protection achieved have been found to be 74-91% and 92-97% at depths of 1000 and 3000 m respectively. The difference in corrosion rates and the degree of protection of the metals at different depths have been attributed to the concentration of dissolved oxygen at those depths.

Though the use of cathodic protection and metallic coatings is believed to be the most effective for controlling corrosion in marine environment, their efficiency depends on factors like water currents, temperature, salinity, dissolved oxygen, pH, and biofouling¹, which are site specific. A number of sacrificial anodic materials are being used for cathodic protection of metals, e.g., mild steel, is protected against corrosion by coupling with alloys of magnesium, zinc and aluminium, whereas, copper can be protected with metals such as mild steel and aluminium². Information on the corrosion behaviour of metals and alloys and their cathodic protection in the oceanic waters is scanty^{1,3}. The present investigation has been, therefore, undertaken to augment the knowledge about factors which would help in developing efficient technology for exploitation of deep sea resources. Corrosion rates for cathodically protected and unprotected mild steel and copper have been estimated by exposing them in deep oceanic waters below 1000 m for one year and is discussed in relation to important physico-chemical parameters.

Experimental Procedure

Commercial grade mild steel (C-0.2%, Si-0.5%, Mn-0.26%, P-0.05%, S-0.04%, Fe-rest) and copper (Ni-0.05%, Cu-rest) panels were used. Each metal was tested in two different sets, one cathodically protected and the other unprotected. For achieving cathodic protection, mild steel was galvanically coupled with commercial grade aluminium (Si-0.15%, Mn-0.8% and Al-rest) whereas, copper was coupled with mild steel and aluminium separately. The cathode to anode

area ratio was 10:1 for all the samples. The panels and sacrificial anodes were cleaned following ASTM standard procedure and weighed before immersion⁴. Two stations each were selected in the Arabian Sea and Bay of Bengal (Fig. 1). The panels were exposed at different depths at each station with the help of deep sea mooring system as described earlier⁵. The depths of immersion were 1100, 1700 and 2300 m in northern Bay of Bengal (site 4) and 1000 and 2300 m in the central Bay of Bengal (site 3). In the Arabian Sea the depths were 1100, 2100 and 3000 m in western Arabian Sea (site 2) and 1700 and 2900 m in eastern Arabian Sea (site 1). The panels were retrieved after one year (Nov. 89-Nov. 90) cleaned and weighed. The loss in weight of each panel and the anode were recorded. The corrosion rate has been expressed as mils per year (MPY). The percentage protection of metal was calculated using the following formula:

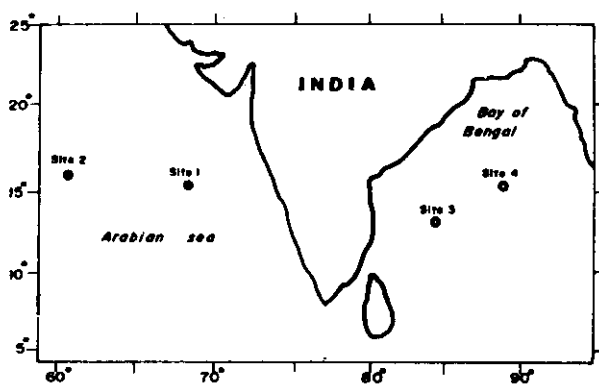


Fig. 1—Station location map

$$\% \text{ protection} = \frac{100(x-y)}{x}$$

where x = corrosion rate of unprotected metal
 y = corrosion rate of protected metal

In addition, water samples were collected from the depths under study for determination of salinity, pH and dissolved oxygen at the time of deployment and retrieval of panels. Reversing thermometer was used for recording water temperature.

Results and Discussion

Physico-chemical parameters—The physico-chemical parameters were found to vary with varying depth. The water temperature in Bay of Bengal varied from 2.1°C at 2300 m to 6.4°C at 1000 m whereas, it ranged from 1.6°C at 3000 m to 5.4°C at 1100 m in the Arabian Sea. The salinity ranged between 34.84 ppt at 3000 m to 35.37 ppt at 1100 m depth in the Arabian Sea whereas, it varied from 34.76 ppt at 2300 m to 34.93 ppt at 1000 m in the Bay of Bengal. The concentration of the dissolved oxygen in the Arabian Sea varied from 0.56 mL/L at 1100 m to 3.18 mL/L at 3000 m whereas, in the Bay of Bengal it varied from 1.0 mL/L at 1000 m to 2.9 mL/L at 2300 m. The pH ranged between 7.8 at 1100 m and 7.92 at 3000 m in the Arabian Sea and from 7.68 at 1100 m to 7.72 at 2300 m in the Bay of Bengal.

Mild steel—The corrosion rate of unprotected mild steel panels increased with increase in the depth of immersion (Fig. 2). These panels were found to suffer with general type of corrosion. The corrosion rates ranged from 1.6 MPY at 1100 m to 2.1 MPY at 3000 m depth in the Arabian Sea and between 1.56 MPY at 1000 m and 2.3 MPY at 2300 m in the Bay of Bengal, i.e., the rate increased by ~31-47%. The dissolved oxygen content was also found to increase with increase in depth. Similar results were found in an earlier study³. The results thus show a close relationship (coefficient of correlation $r=0.87$ to 0.90) between the corrosion rate and dissolved oxygen concentration. Coefficient of correlation was calculated using following formula:

$$\text{Coefficient of correlation } (r) = \frac{\sum xy - n\bar{x}\bar{y}}{n\sigma_x\sigma_y}$$

$$\bar{x} = \frac{\sum x}{n}$$

$$\bar{y} = \frac{\sum y}{n}$$

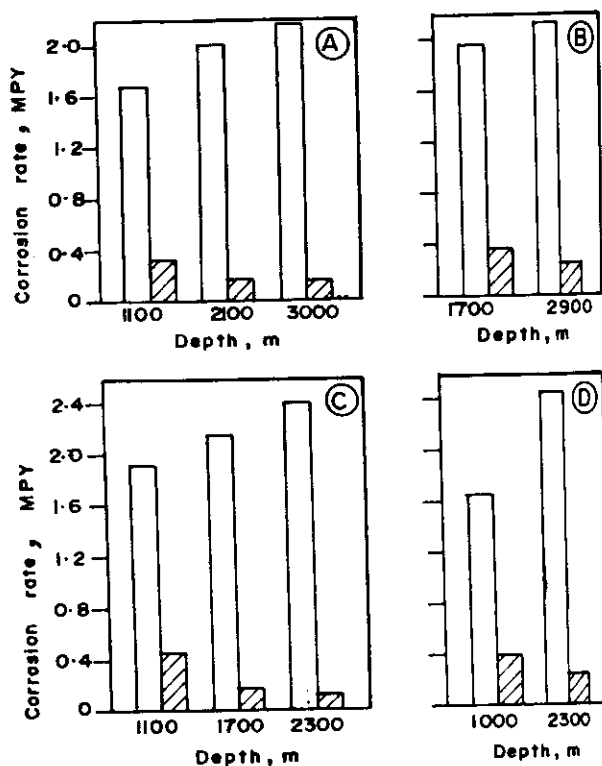


Fig. 2—Variation of corrosion rates of cathodically unprotected (□) and protected (■) mild steel at different depths in western (A) and eastern (B) Arabian Sea and in northern (C) and central (D) Bay of Bengal

$$\sigma_x = \frac{\sqrt{\sum (x - \bar{x})^2}}{n}$$

$$\sigma_y = \frac{\sqrt{\sum (y - \bar{y})^2}}{n}$$

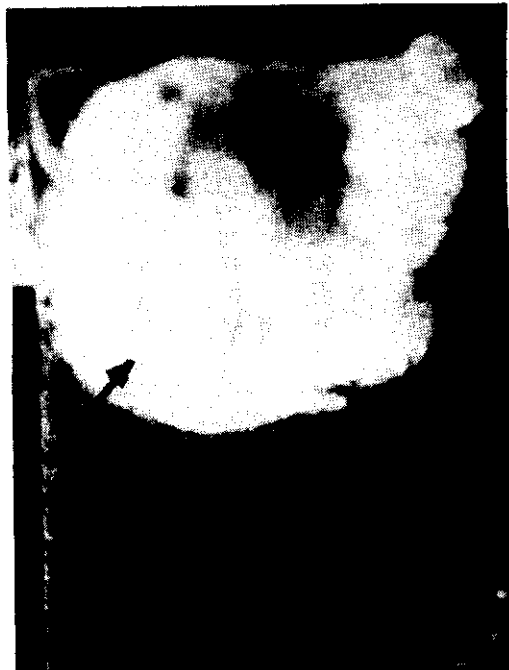
where

x = value of dissolved oxygen concentration

y = value of corrosion rate

n = number of values

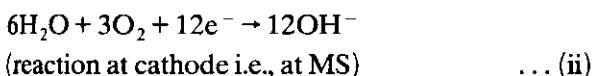
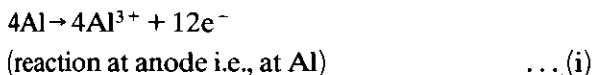
On the other hand the corrosion rate of cathodically protected MS below 1000 m was found to increase with increase in depth (Fig. 2) and ranged between 0.14 to 0.34 MPY in the Arabian Sea, and between 0.12 to 0.44 MPY in the Bay of Bengal. The trend of the corrosion of protected panels was just reverse to that of unprotected panels, i.e., the percentage protection of metal was found to increase with increased depth. A minimum of 75% protection was observed at 1000 m depth and a maximum of 94% protection was observed at 2300 m depth in the Bay of Bengal. In the Arabian Sea the values were 81 and 93% at 1100 and 3000 m, respectively. The difference in



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Fig. 3—Photograph of Al anode on mild steel showing flaky corrosion product

corrosion rate of protected MS at various depths may be attributed to the difference in the extent of loss of anode material. The aluminium anodes as can be seen in the Fig. 3 produced a adherent flaky product which was milky-white and covered the whole anode surface. The increase of percentage protection below 1000 m is associated with the increase of per cent loss of anode material and dissolved oxygen concentration (Table 1). It is therefore, assumed that the oxygen which is the important cathodic reactant as per the reaction (ii) might have promoted the cathodic reaction at greater depth, thereby, causing greater loss of anode and hence higher protection to the cathode.



Earlier³ it was observed that the corrosion rate of unprotected aluminium decreases with increase of immersion depth in deep oceanic waters. The decrease of corrosion rate at greater depth could be attributed to the higher amount of dissolved oxygen which is responsible for forming protec-

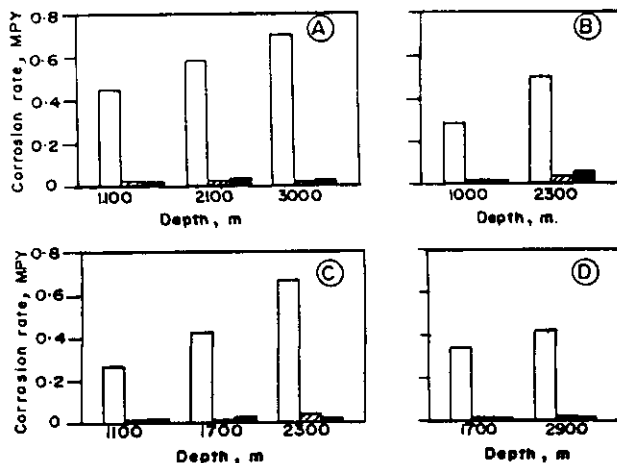
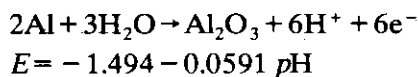


Fig. 4—Variation of corrosion rates of cathodically unprotected (□) and protected (with MS—anode ▨ and Al—anode ■) copper at different depths in western Arabian Sea (A), central (B) and northern (C) Bay of Bengal and eastern Arabian Sea (D)

tive oxide film. However, the present study indicated that aluminium anode underwent higher dissolution at greater depth. The possible explanation to this effect could be given based on the hypothesis proposed by Deltombe and Pourbaix⁶. According to them aluminium gets oxidised in water by following reaction.



One H^+ is formed for each electron. If the hydrogen ions accumulate, the pH become very low and the protective oxide film would get dissolved.

Copper—Like mild steel unprotected copper panels also exhibited increase of corrosion rate at depths greater than 1000 m (Fig. 4). General type of corrosion was observed in all the panels. The increase may be attributed to the higher concentration of dissolved oxygen. The corrosion rates in the Bay of Bengal varied from 0.24 to 0.63 MPY whereas, in Arabian Sea the rates ranged between 0.33 to 0.67 MPY, i.e., the corrosion rate at greater depth increased by 103-162%. These rates were 3-7 times lower than that of MS. The corrosion rates for cathodically protected copper were found to range between 0.015 to 0.04 MPY, irrespective of the type of anode, i.e., approximately 92-97% protection was achieved. Like MS, the protection of copper was found to increase with increased depth. Both MS and Al anodes were found to perform well and provided almost the same degree of protection to copper. In this case also the increase of protection of ca-

Table 1—Variation of physico-chemical parameters, percentage cathodic protection and percentage weight loss of anode material at various depths in deep oceanic waters

A	B	C	D	E	F	G	H	I	J	K	L
Site 1	1700	3.25	35.00	2.15	7.84	82	11	93	31	93	25
	2900	1.72	34.83	2.99	7.89	88	12	95	41	96	53
Site 2	1100	5.40	35.37	0.56	7.80	81	9	95	23	95	48
	2100	2.50	34.95	2.70	7.87	91	16	96	76	92	64
	3000	1.60	34.84	3.18	7.92	93	18	97	78	97	66
Site 3	1000	6.40	34.93	1.00	7.68	75	10	92	32	92	18
	2300	2.25	34.76	2.90	7.72	89	16	94	66	93	38
Site 4	1100	5.91	34.90	1.50	7.68	75	12	93	22	93	29
	1700	3.19	34.82	2.40	7.70	92	11	96	58	93	38
	2300	2.10	34.78	2.90	7.72	94	17	97	77	97	46

A: Exposure site; B: Depth(m); C: Temp ($^{\circ}\text{C}$); D: Salinity (ppt); E: Dissolved oxygen (mLL^{-1}); F: pH; G: % protection by Al anode to MS; H: % Al anode wt. loss on MS; I: % protection by MS anode to copper; J: % MS anode wt. loss on copper; K: % protection by Al anode to copper; L: % Al anode wt. loss on copper.

thode was associated with the increase in percentage weight loss of both type of anode materials and dissolved oxygen concentration. This shows that better the dissolution of an anode material higher the protection⁷.

Conclusion

Therefore, it can be concluded that both aluminium and mild steel anodes performed well and equally for the protection of mild steel and copper at greater depths. Aluminium theoretically possesses an adequate potential and very high current output for use as sacrificial anode. However, the utility of pure aluminium has not yet been realised successfully because of a protective oxide film formation on its surface⁸. Moreover, corrosion rate of unprotected mild steel and copper increased with increase of immersion depth below 1000 m whereas it decreased with increase of immersion depth below 1000 m for protected mild steel and copper. Dissolved oxygen appears to be one of the important factors for this change. A linear relationship was observed between the loss of anode materials and the amount of protection to cathode.

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