Galvanic corrosion behaviour of Al, mild steel, stainless steel and Zn coupled to Cu in seawater

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The change in area ratios considerably alters the behaviour of passive metals. The passive metals, Al and stainless steel experience ennoblement of galvanic potentials due to the formation of thin microbial film. The coupling of Cu and type 304 stainless steel in natural seawater is detrimental to both. Galvanic potentials, current and corrosion rates of metals are affected by the formation of corrosion products, calcareous deposits and biofouling attachments.

Presence of liquid electrolyte at the junction of galvanically dissimilar metals or alloys can aggravate the corrosion process. Galvanic behaviour of metals and alloys in seawater, from short term tests, is known. However, data from long term tests are sparse. Thermodynamic equilibrium existing at the metal/electrolyte interface is altered when the metal is electrically connected to a galvanically less active metal. With increased duration of exposure, the simple system of metal/seawater interface can assume more complex behaviour due to the formation of corrosion products, calcareous deposits and biofouling attachments. Present study deals with current/potential characteristics of Al, mild steel, stainless steel and Zn coupled to Cu with different area ratios for 45 days in natural seawater.

Materials and Methods
Commercially available metals and alloys in the form of 2 mm thick rolled sheets were used in this study. Cu panels of 75 mm × 75 mm size were used as cathode members for all the couples. The cathodic to anodic area ratios employed were 1.5, 3 and 9. Appropriate size panels were mechanically polished, degreased with acetone and galvanically coupled using multistrand copper wires (the joints were insulated using Americo lacquer). Couples were positioned in specially designed frames so that they faced each other vertically in tanks filled up with natural seawater. The tanks were recharged with fresh natural seawater once every 48 h.

Galvanic currents of the couples were measured using zero resistance ammeter, and the galvanic potential with respect to saturated calomel electrode (SCE) using high impedance digital voltmeter. Visual observations of the surfaces of the couples were also recorded. During the experimental period, 4 withdrawals were made. The weight gain effected by the micro-biological slime and calcareous deposits was determined after drying the panels at 60°C for 1 h. The gravimetric corrosion rates of the metals were determined after pickling in recommended solutions to facilitate removal of corrosion products.

Results and Discussion
The ennoblement of the open circuit potential (OCP) of the Al uncoupled may be associated with passivation; while the galvanic potential of coupled Al exhibits overall trends towards active values as time proceeds (Fig. 1). Low corrosion rate of the Al control is observed (Fig. 2) and this appears to be associated with the ennoblement of potential due to the synergistic effect of passivation and microbial slime formation. On the other hand, coupled Al encounters accelerated sacrificial dissolution in all cases. The deviation in galvanic potential from 0.1 M NaCl solution is probably determined by the cathodic processes like O₂ reduction and calcareous deposit formation.

The galvanic potentials of Type 304 stainless steel (coupled to Cu) in seawater at all 3 area ratios were in the active region compared to the OCP of the uncoupled stainless steel (Fig. 1). The OCP of 304 stainless steel of about −0.1 V (SCE) conforms well with the values reported in the literature while it is about −0.36 (SCE) in 3% NaCl solution. The ennoblement of galvanic potentials is the result of formation of thin microbial film. However in the case of higher area ratios of passive metals, the film
being not tenacious has given effect to numerous tiny pits, resulting in higher corrosion rates during the first 20 days of the test. It is evident that the bio-film got thickened and shielded the metal from corrosion as the test duration increased (Table 1). The unstability of the passive film in the higher area ratios made it difficult to assess the effect of area ratios. The behaviour of 1.5 area ratio of both the systems, Al-Cu and stainless steel-Cu couples are in agreement with

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<th>Couple</th>
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<th>Area ratio</th>
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<tr>
<td></td>
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<td>1.5  3.0  9.0</td>
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<tr>
<td>Al vs Cu</td>
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<td>Stainless steel vs Cu</td>
<td>Stainless steel</td>
<td>0.002 0.004 0.005</td>
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* Control data for 10 days not available  a = Green corrosion product was observed  b = Presence of green algae recorded
the values reported\(^1\). The corrosion rates of all the coupled panels were higher than the control panels and decreased as the test duration increased.

Ennoblement of galvanic potentials portray the extent of polarization during the anodic dissolution of metals. The corrosion rate of Zn increases with the increase in area ratio, whereas over the period of exposure it has a fall, and the fall is more pronounced in area ratio 9 (Fig.2).

The corrosion rates of galvanically coupled Cu to Al or Zn are less than that of the uncoupled Cu (Fig.3). The corrosion of Cu coupled to aluminium or Zn could be due to the ennoblement behaviour and passive film formation\(^1\) on Al, corrosion product and calcareous deposits on Zn. In Cu-stainless steel couple, the corrosion rates of individual metals are higher than that of uncoupled Cu and stainless steel (Figs 2 and 3). This could be due to the ennoblement behaviour of stainless steel caused by microbial film formation\(^1\) and the adherent corrosion products on Cu (Table 1).

Fig.4 depicts the linear increase in anodic current density with respect to area ratio for mildsteel, but it shows a decrease as duration of exposure extends. Fig.4 shows that for passive metals and alloys (mostly) the current density increases initially and after some time shows a considerable decrease. This is most pronounced for the 2 higher area ratios.

The biomass (inclusive of calcareous deposit) adhered on each set of panels is presented in Table 1. The accumulated mass of the anodic metal increases as the area ratio increases and the reverse happens in cathodic metal surfaces. During the initial period of exposure the dissolution rate of anodes is in the ascending order as the area ratio increases and this gets impaired as the duration extends, by the formation of calcareous deposits on the cathodic members of the couple and also the formation of adherent corrosion product films on the anodes which may be responsible for the reduction in micro galvanic action.

The galvanic behaviour of mild steel-Cu system studied elsewhere conforms well with the present study\(^8\). It is concluded that the change in area ratios considerably alters the behaviour of passive metals.

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**Fig. 3**—Corrosion rates of Cu panels coupled to Al, stainless steel and Zn in seawater

**Fig. 4**—Galvanic current density of Fe-Cu (A) and stainless steel-Cu (B) couple in natural seawater
Coupling of Cu and type 304 stainless steel in waters with bacterial activity is detrimental to both and calcareous deposit and biofouling preferentially occur on the cathodic members of the galvanic couples.

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References