

# An accelerated study to evaluate the performance of coated concrete and bare concrete reinforcement exposed to the sea

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**R**EINFORCED concrete test specimens with embedded steel rebars coated with metallic, organic and inorganic protective coatings were exposed in the splash zone; test specimens with bare steel rebars were also included for comparison. The test was accelerated by adopting weak concrete design parameters compared to the recommended ones for marine structures. Half-cell potentials were periodically recorded by the single electrode method during the test. At the end of the test period, the specimens were split and comparison measurements such as areas covered with rust, depth of pits and weight loss were carried out. The rusted steel rebars were subjected to mechanical tests to evaluate percentage reduction in mechanical properties. Results are drawn from these observations.

Embedded steel rebars coated with cadmium and cement slurry (containing anodic inhibitor) were found to have performed exceptionally well. Zinc on the steel rebar delayed rapid corrosion and consequent cleavage of concrete cover. The cadmium-plated steel rebar appeared practically safe from corrosion attack after 10 months' exposure. The corrosion rate of galvanized steel was 0.06mm/yr at the end of 10 months' exposure, with its entire surface covered with brown rust; for the cement-slurry coated steel rebar, 56% of the surface was covered with brown rust and the corrosion rate was also 0.06mm/yr at the end of 10 months' exposure. The bare steel recorded the highest corrosion rate of 0.15mm/yr, with almost its entire length becoming covered with brown rust at the end of 4 months' exposure.

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## Introduction

Corrosion of embedded steel in reinforced concrete (RCC) structures leading to cracking and subsequent spalling is now recognized as a major problem confronting the construction industry in almost all parts of the world[1]. This problem is severe in coastal and offshore RCC structures because of the presence of aggressive chloride ions in seawater. The emphasis of the research reported here is on the development of suitable remedial methods to control the corrosion of the embedded steel in concrete. Some of the remedial measures for controlling corrosion of the embedded steel include application of protective coatings and inhibitors on the surface of the embedded steel bars[2]. Many conflicting findings have been reported in the literature on the performance of galvanized embedded bars in a marine environment[3], whereas cadmium is reported to be unaffected under high chloride concentrations[4]. Among organic protective coatings, epoxy coatings were reported to perform satisfactorily as long-term reliable protective coatings on embedded bars under the direct intrusion of seawater[5]. Reports

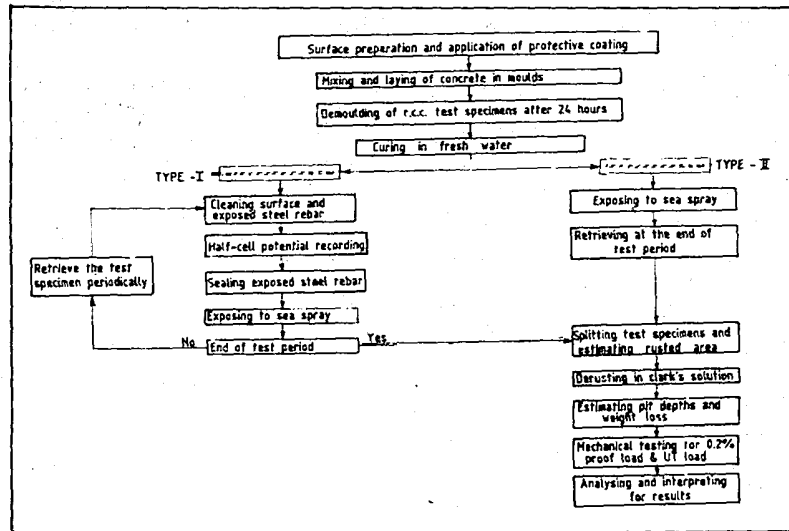
are also available in which asphalt, chlorinated rubber and vinyl paints have been tried as organic protective coatings on the embedded bars[6]. Corrosion inhibitors are not widely used in marine RCC structures; however, it is reported that sodium nitrite is being used in Europe[7] for this purpose.

The present paper discusses the relative performance of the bare and protective-coated steel rebars embedded in concrete. Selection of the metallic, organic and inorganic protective coatings was based on the local interest. The results are based on field studies carried out in the splash zone of the sea; to accelerate the study, the following procedures were adopted:

- (i) the test specimens were exposed to sea spray;
- (ii) a relatively-weak set of concrete parameters were adopted for the test specimens in place of the recommended concrete parameters for offshore structures.

A few test specimens with plain embedded steel were exposed to both sea spray and the inter-tidal zone of the sea for evaluation of comparative performance.

Fig.1. Methodology of the experiments.



### Experimental investigation

The experimental work is based on field studies carried out by exposing the test specimens to sea-water spray at a selected location off the National Institute of Oceanography, Goa. Half-cell potentials were periodically recorded for all individual test specimens during the exposure period. The field test specimens were divided into two groups, the first one being immersed for approximately 4.5 months and the other for approximately 10 months. At the end of each exposure period the specimens were broken, and the embedded steel bars were subjected to visual observations, complementary measurements, weight loss measurements and mechanical strength evaluation.

The steps involved in the experimental work are shown in Fig. 1.

#### Preparation of test specimens

TOR-50 steel conforming to IS-1786 (BS-4461)

was used as embedded steel for the specimens; Table 1 gives the mechanical and metallurgical properties of the steel and concrete. The adhering rust was removed by dipping in Clark's solution prepared as described in the ASTM specification [8]. Table 2 gives details of the different types of protective coatings employed in the present study.

A wooden mould (shown in Fig. 2) was used to prepare the prism-shaped test specimens. This mould was designed to locate and hold in position the embedded steel bar to the desired clear concrete cover thickness. The test specimens were demoulded after 24 hours, and immersed in fresh water for curing. Two different types of test specimens were prepared, as shown in Fig. 3. In one, the embedded steel bar was projected 10mm out of the concrete to facilitate the half-cell potential measurement with the single electrode method. The dimension of all the specimens was 44mm × 44mm × 536mm.

Table 1. Properties of embedded steel and concrete.

Item			Specification							
Embedded steel bars	iii)	Physical properties	8mm diameter TOR-50 steel Area of the lug and rib: 2.584mm <sup>2</sup> /mm length							
	iii)	Surface state	Hot-rolled, cold-twisted and covered with brown rust							
	iii)	Mechanical properties	Average 0.2% proof load: 28065kg Average ultimate tensile load: 3347kg Average % of elongation: 15.25% Average modulus of elasticity: 2.17 × 10 <sup>4</sup> kg/mm <sup>2</sup>							
	iv)	Chemical composition (% by weight)	<table border="1"> <thead> <tr> <th>C</th> <th>Mn</th> <th>P</th> <th>S</th> </tr> </thead> <tbody> <tr> <td>0.21</td> <td>0.56</td> <td>0.048</td> <td>0.04</td> </tr> </tbody> </table>	C	Mn	P	S	0.21	0.56	0.048
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0.21	0.56	0.048	0.04							
Concrete	iii)	Design parameters	Mix ratio: M150 (1:2:4) Water-cement ratio: 0.8 (by weight) Clear concrete cover thickness: 18mm							
	iii)	Concrete ingredients	Cement: Portland pozzolona with fly ash as pozzolonic material. Fine aggregate: Calcareous medium sand, with coefficient of curvature (Cu) = 2.5 Coarse aggregate: crushed granite between 5-10mm							

**Table 2. Protective coatings and their details of application.**

Type of protective coating on rebar	Surface preparation on embedded steel	Coating/plating detail
Cadmium	Pickling in Clark's solution for 1-3 minutes	Electroplating in cyanide bath to 50-55 microns thickness.
Zinc	Pickling in 25-30% HCl followed by dipping in alkali solution.	Electroplating in cyanide bath to 25-30 microns thickness.
Passivated zinc	Pickling in 25-30% HCl followed by dipping in alkali solution	Electroplating as above. After electroplating the surface was passivated by dipping in 0.2% potassium dichromate solution for 15-25 seconds. Final coating thickness was 25-30 microns.
Alkyd resin	Pickling in Clark's solution for 1-3 minutes	A primer coat of red oxide to 22 to 40 microns thickness. After drying a final coat of alkyd resin to a thickness of 22 to 32 microns.
Cement slurry (Portland pozzolona, Narmada cements)	Pickling in Clark's solution for 1-3 minutes	Steel rebars were dipped in cement slurry prepared in the following proportions: 100gm cement + 40gm water + 2gm $\text{Na}_3\text{PO}_4 \cdot 2\text{H}_2\text{O}$ .
Resin in cashewnut shell liquid (CNSL) ( <i>Anacardium occidentale</i> Linnaeus)	Pickling in Clark's solution for 1-3 minutes	Condensate product obtained by boiling CNSL and formaldehyde in 1:1 ratio for 1.5 hours was painted for 500-550 micron thickness over redoxide primer.
Zinc chromate (British paints)	Pickling in Clark's solution	A coat of zinc chromate to 22 to 35 microns thickness.

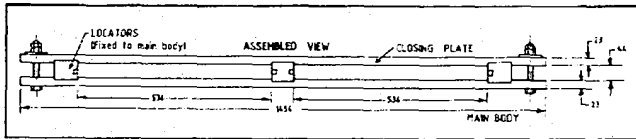


Fig.2. Concrete specimen mould.

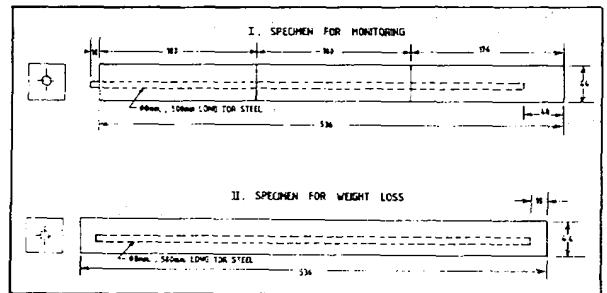


Fig.3. Reinforced concrete test specimens.

#### Exposure of the test specimens and data collection

In the field, the test specimens were mounted in fibre-reinforced plastic tanks with drain holes as shown in Plate 1. The sea-water spray was very severe during the SW monsoon period.

The engineering data and observations recorded during the step-by-step field study were as follows:

#### I: Data recorded before splitting the test specimens

Half-cell potential data was periodically recorded during the course of exposure of the specimens to seawater spray. For the half-cell potential measurements, the electrical circuitry details are basically as the ASTM specification[9]; however, instead of  $\text{Cu}/\text{CuSO}_4$  reference electrode, a saturated calomel electrode was used as reference electrode. The contact surface of the agar-agar salt bridge was modified as shown in Fig. 4. The maximum value of the half cell potential was noted on all the four faces of the test specimens.

#### II: Data/observations recorded after splitting the test specimens

- (a) Wight loss data for embedded steel bars was recorded to assess corrosion rates; Fig. 1 shows the steps involved in this measurement.
- (b) Complementary measurements were carried out on the rusted embedded bars after splitting the specimens. Data on parameters such as area covered with black/brown rust and pit depths were

- noted for each steel bar individually. A point micrometer with a  $15^\circ$  tapered measuring end was used for estimating the depth of pits.
- (c) Mechanical tests were carried out on each individual rusted embedded steel bar to obtain data on reduction at 0.2% proof load and ultimate breaking load.
- (d) Observations were carried out on the location of the fracture zone to find the effect of pit size and its configuration.

Plate 1. Exposure of tests specimens in the splash zone.



**Table 3. Performance of protective coatings based on half-cell potential measurement.**

Test specimen	Half cell potential data: no. of days to exceed -290mV SCE
Plain embedded steel in splash zone.	6 days (-310mV)*
Plain embedded steel in intertidal zone.	16.5 days (-306mV)
Alkyd-resin painted embedded steel	3.5 days (-306mV)
Cement-slurry coated embedded steel	10.5 days (-295mV)
Zinc-chromate painted embedded steel	9 days

\*Measured half-cell potential

**Results**

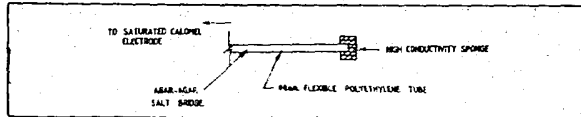
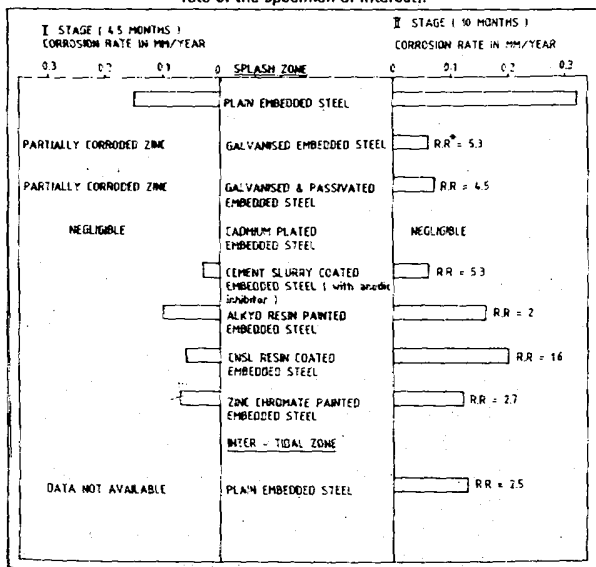
*Half-cell potential measurements*

Based on the ASTM-876C criterion, the number of days taken by the different protective-coated embedded steel rebars to attain the potentials corresponding to 90% corrosion probability were noted and are given in Table 3. The cement-slurry coated steel rebars took 10.5 days to attain this potential after exposure in the splash zone. This value happens to be the maximum, while the bare steel rebar took only 6 days and 16.5 days in the splash and intertidal zones respectively.

*Corrosion rate by weight loss method*

Fig. 5 shows the corrosion rates expressed in mm/year for steel rebars coated with different protective coatings. The bare steel rebar in the splash zone recorded the highest rate of corrosion at 0.15mm/yr and 0.32mm/yr in 4.5 months' and 10 months' exposure respectively, whereas bare steel rebar in the intertidal zone recorded a corrosion rate of 0.13mm/yr in 10 months' exposure, which is moderate. The corrosion rate for the galvanized

**Fig. 5. Maximum values of corrosion rates obtained by the weight-loss method. Retardation ratio = (corrosion rate of base steel in splash zone)/(corrosion rate of the specimen of interest).**



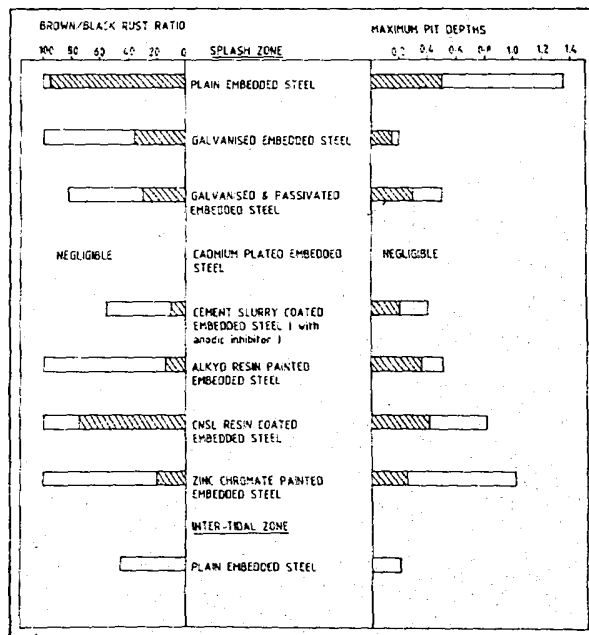
**Fig.4. Modified salt bridge for SCE.**

steel rebars after 4.5 months' of exposure could not be calculated because of local corrosion of the substrate steel at many points; however, the corrosion rate of the substrate steel after 10 months' exposure was 0.06mm/yr. For cadmium plated steel, the weight loss was to the extent of 10mg after 10 months' exposure. For cement-slurry coated steel rebars, the corrosion rate was 0.03 and 0.06mm/yr after 4.5 months' and 10 months' exposure respectively. For other steel rebars coated with organic protective coatings, the corrosion rates recorded were higher than those for cement-slurry coated steel rebars, but they were found to be lower than bare steel rebars.

*Brown/black rust ratio and pit depth*

Fig. 6 shows the brown/black rust ratios and pit depths for steel rebars coated with different protective coatings. The bare steel rebars in the splash zone were found to be covered with thick brown rust on their entire length, while the steel rebar in the intertidal zone was found to be rusted locally. For galvanized steel rebars 35.5% of the surface was covered with brown rust after 4.5 months' of exposure, while at the end of 10 months' of exposure, the entire surface was covered with a thin layer of brown rust. The cadmium plated steel rebar was least affected, but tiny black patches of cadmium chlorides were found at a few locations.

**Fig.6. Maximum values of rust ratios and pit depths.**



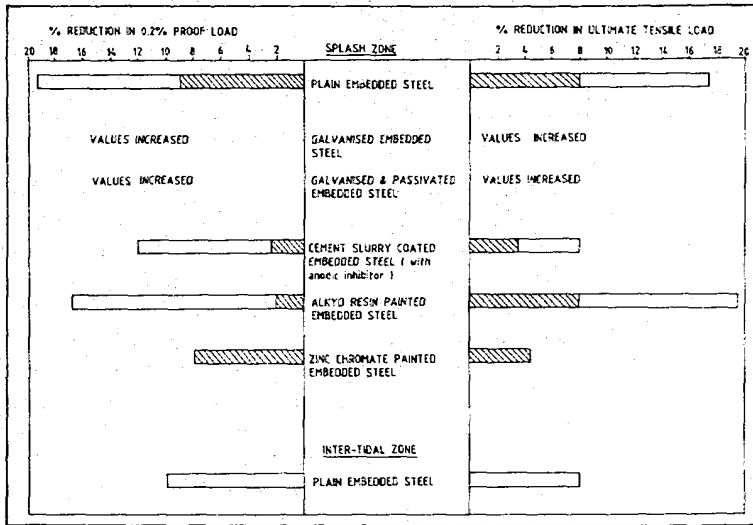


Fig.7. Maximum values of % reduction in mechanical properties.

For alkyd-resin painted and zinc-chromate painted steel rebars, the rusted area was found to be 65%. The blisters formed due to corrosion of the base steel caused paint failure on the alkyd-resin and zinc-chromate painted surfaces, while in the case of CNSL resin, flaking of the paint coat was a common observation. All the organic protective coated embedded steel rebars were completely covered with brown rust after 10 months' of exposure, but the cement-slurry coated steel rebars performance was superior, showing 10% and 56% as rusted areas in 4.5 months and 10 months respectively.

Minimum pit depths were observed in the galvanized steel rebars, followed by cement-slurry coated steel rebars.

#### Mechanical testing

Fig. 7 shows the result of mechanical testing carried out on the rusted steel rebars. There was an appreciable reduction of 19.4% in 0.2% proof loads and 17.4% in ultimate tensile loads of bare steel rebars in the splash zone. Galvanized steel rebars

recorded substantial increased 0.2% proof load and ultimate tensile loads compared to their rated load values. For the cement-slurry coated steel rebars, the percentage reductions in 0.2% proof load were 2.4 and 12.4 in 4.5 months' and 10 months' exposure respectively, while the percentage reductions in ultimate tensile load were 3.6 and 8 in 4.5 and 10 months' exposure. Other organic protective coated rebars recorded moderate values.

All the steel rebars failed in the ductile mode of failure, except those of galvanized steel which failed by a typically brittle mode of failure exhibiting distinctive 'river' lines as shown in Plate 2. There was no 'necking' near the fractured surface. The fracture in all cases was found to be initiated nearer to fine pits, although the few discrepancies observed in the results presented here are attributed to uneven compaction and segregation of the concrete.

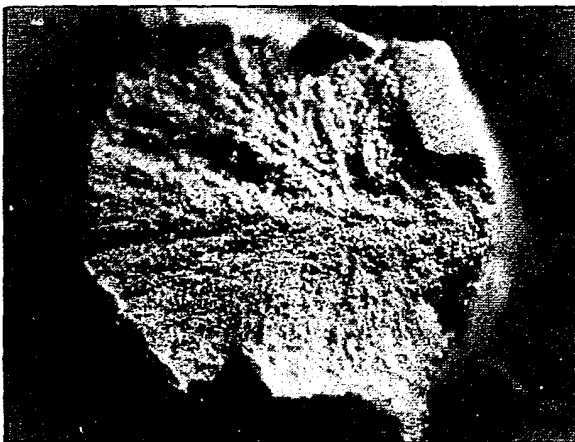
#### Discussion

The present investigation is in line with accelerated studies suggested by Capp[10], assuming that the protective coatings giving satisfactory results in such accelerated studies would provide satisfactory corrosion resistance under the actual concrete parameters recommended for marine structures.

The results based on half-cell potential data in Table 3, though qualitative in nature, can be interpreted in association with other results to show that the performance of the cement-slurry coating is superior. The results are drawn after confirming good correlation between the externally-measured half-cell potentials and the extent of rusting of the steel rebar with the present set of concrete parameters.

In all the steel rebars exposed in the splash zone, the corrosion was of a general nature due to the

Plate 2. Cross-sectional view of steel rebar failure in the brittle mode.



general loss of passivity as a result of excessive amount of chlorides. Initially, corrosion was localised due to the formation of local alkali concentration cells along the steel rebar; this was evidenced by the large potential gradients. Later on, the potentials settled to around -600mv SCE. pH measurement of the concrete surrounding the corroded and the uncorroded steel rebar samples confirmed the formation of alkali concentration cells. For the specimens in the intertidal zone, the entire corrosion process is dependent on the diffusion of chlorides, dissolved oxygen and carbon dioxide through the saturated concrete. Lack of oxygen was evidenced by the formation of black and comparatively less expansive magnetite ( $\text{Fe}_2\text{O}_3$ ). The sea water reaching the steel surface becomes rich in alkalinity due to dissolution of the previously-formed calcium hydroxide, and thus the bar is locally subjected to rust.

The cement slurry with anodic inhibitor provided enough alkalinity in the pore water surrounding the steel rebar. This delayed the chloride ion activity from reaching the threshold value (0.6 times the hydroxyl ion activity) and initiating corrosion. But even after the initiation of corrosion due to local depassivation, the fresh seawater entering the concrete brought enough alkalinity from the nearby concrete, and once again restored the passivity. Thus, the pit depths and rusted areas are low because the depassivated surfaces were being passivated at a faster rate.

The paint coat of CNSL resin lacked the required amount of toughness. The paint coat cracked and flaked even with a low volume of rust forming beneath it. This paint formulation needs to be modified to improve its elastic properties.

Galvanizing, though not protecting the substrate steel, certainly delayed its corrosion. The corrosion rate of the substrate steel was only 0.06mm/year after 10 months' exposure, which is insignificant in any design. The brown rust was thin, and thus the time to spalling of concrete would also be delayed. The brittle mode of failure of the galvanized steel rebar during mechanical testing was due to acid pickling prior to electroplating. This transition of mild steel from the ductile to the brittle state is attributed due to the phenomenon of hydrogen embrittlement.

In all the steel rebar the cracking was found to have been initiated from the base of very fine pits or from unruled surfaces. The deep pits were scallop-shaped, while the fine pits were very sharp, thus acting as zones of high stress concentration for crack initiation.

### Conclusions

The conclusions drawn from the present investigation are:

1. The galvanized embedded steel is superior to bare steel rebars after both 4 and 10 months' exposure. Galvanizing did not provide complete protection to steel after 10 months' of accelerated testing.
2. Cadmium-plated embedded steel was not affected by the sea environment, even after 10 months' exposure.
3. Cement-slurry coated embedded steel (containing anodic inhibitor) performed fairly well in the 4.5 months' test, but only fared moderately under 10 months' exposure.

### Acknowledgements

The authors are grateful to the Head OED of NIO and the Director of NIO for their encouragement.

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