Cement & Concrete Composites 26 (2004) 235–242

Cement & Concrete Composites

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Studies on the performance of migratory corrosion inhibitors in protection of rebar concrete in Gulf seawater environment

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Abstract

In recent years, migratory corrosion inhibitors (MCI) have been suggested as the possible chemicals for rehabilitating the damaged reinforced concrete structure. The inhibitor migrates through the concrete to the reinforcing steel and protects it from further corrosion by providing a thin, protective coating of MCI-molecules on steel reinforcement. Studies have been carried out to investigate the performance of dimethyl ethanol amine based MCI-A and triethanol amine based MCI-B as surface coatings. Reinforced concrete specimens coated with MCI-A and MCI-B were subjected to exposure tests in salt solutions. The tests were consisted of immersing the specimens in 5% NaCl solutions (laboratory tests) and open seawater or exposing the specimens to high tide (splash zone) for periods ranging from 6 to 12 months. The condition of the exposed specimens was evaluated by physical examination of the rebar and also by carrying out electrochemical measurements. The electrochemical studies were consisted of open circuit potential and polarization measurements. The experimental data from the studies have been analyzed and the usefulness of MCI in protecting the rebar concrete is discussed.

Keywords: Corrosion inhibitors; Rebar concrete; Seawater; Gulf

1. Introduction

The failure of concrete structures, because of the corrosion of reinforcing steel in presence of chloride environment, is a familiar phenomenon to building industry. The failure of concrete structures in Gulf coastal region is more pronounced due to the carried over chloride ion air-borne salts or high chloride in soil. Chloride destroys protective oxide layer on steel rebar and the corrosion initiates. As corrosion progresses, copious oxide builds and cause expansion resulting in disbondment of rebar and ultimately failure of the structure. In recent years, migratory corrosion inhibitors (MCI) have been suggested as the possible chemicals for rehabilitating the damaged structure.

MCIs have been developed with the objectives of migration through concrete in order to reach and protect the internal reinforcements even when in an advanced state of corrosion. The diffusion of MCI molecules through concrete pores has been demonstrated and measured utilizing the radioactive isotopes and sensitive electrode techniques. MCIs are proprietary blend of surfactants and amine salts in a water carrier. These inhibitors can be applied on concrete surface or used as concrete admixture.

In recent years, a number of papers appeared in literature showing effectiveness of MCI's [1–3]. A study was carried out to evaluate the anticorrosion systems in the maintenance, repair and restoration of structures in reinforced concrete using MCIs [4]. Measurements of corrosion potentials in laboratory tests and on-site monitoring demonstrated the MCI molecules effectiveness in protecting steel rods from corrosion even in the presence of high concentrations of aggressive salts particularly chlorides. Bjegfovic and Miksic [5] studied MCI using as admixture in fresh concrete mix and as an impregnator on concrete specimen. Based on the data from these studies, it was concluded that MCIs are compatible with concrete and effectively delay the onset of corrosion.

In this paper, the results of a study concerning with the corrosion behavior of reinforced concrete in presence of MCI in marine environment have been described. The environment is consisted of natural seawater and brine (5% NaCl). The results of MCI's have been compared with a volatile corrosion inhibitor.

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doi:10.1016/S0958-9465(03)00042-8

2. Materials

2.1. Inhibitors

Corrosion inhibitors MCI-A and MCI-B and volatile corrosion inhibitor VCI-C were used during the experiments. MCI-A and MCI-B were dimethyl ethanol amine and triethanol amine based inhibitors, respectively, containing propriety blend of surfactants and amine salts in a water carrier. VCI-C was tolyltriazole based vapor based inhibitor.

2.2. Concrete specimen preparation

Type I ordinary portland cement (OPC), sand and aggregates were procured locally. Concrete mixes were prepared using ASTM Type I (OPC) cement with and without inhibitor coating. Concrete mixes were prepared using the following quantities of materials per cubic meter of concrete.

Cement (kg)	Free water (kg)	Cement/water ratio	Sand (kg)	3/8" aggregate (kg)	Admixture (l)	MCI (l)
385	150	0.4	653	1160	6	0.7

After 24 h of setting the samples were removed from the molds and cured in tap water for 28 days. The important properties of fresh concrete at ambient temperature (25 °C) were:

Initial slump	Air content	Unit weight
230 mm	2.3%	2388 Kg/m^3

2.3. Reinforcement bars

To rebar the concrete samples, carbon steel rebars were cut in two sizes: length of the rebars for the samples to be tested electrochemically was kept 200 mm while for tidal zone immersion tests it was 150 mm. Rebars were cut with the silicon carbide cutting wheel, machined, polished, washed with ethanol and dried. For specimens to be tested electrochemically, 3/5 portion of the rebar (120 cm) was encased in the concrete whereas 2/5 portion (80 cm) was exposed to atmosphere. The exposed portion was coated with coal tar epoxy. The length and internal diameter of the molds were 150 and 75 mm, respectively. Rebars coated at the ends were fixed in the center of the molds with the help of clamps provided at both ends of the mold and concrete mixes were casted in. Fig. 1 shows a photograph of casting of concrete mixer in the molds.

In total, 126 uncoated and coated concrete specimens were prepared for the tests. These specimens in coated and uncoated conditions were used for immersion tests in seawater and 5% NaCl solution and open air exposure tests in tidal zone. The inhibitors MCI-A and MCI-B (in liquid form) were applied as a coat on the concrete sample using a brush. Another inhibitor, belonging to vapor phase type, VCI-C was used as a coating on a group of rebars in concrete casting of a number of specimens.

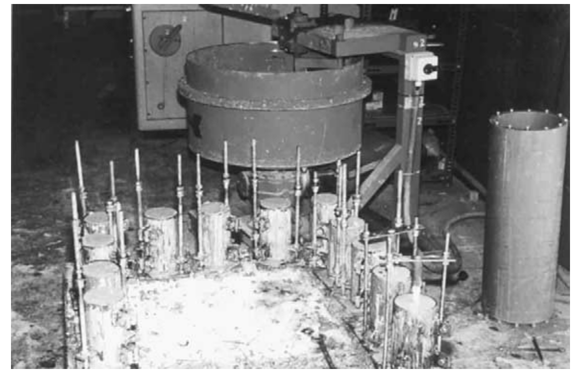

Fig. 1. Photograph showing casting of concrete mixes in the molds.

3. Techniques

3.1. Potentiodynamic polarization studies

The electrochemical behavior of the concrete was studied by potentiodynamic polarization technique using a computer controlled EG & G Model 273 potentiostat. The cylindrical concrete specimens were partially immersed in 5% NaCl and seawater stored in plastic containers. Saturated calomel electrode (SCE) as reference and stainless steel mesh as counter electrodes were used. The experiments were programmed to polarize the specimen potential to about +20 mV vs. open circuit potential (OCP) in both the directions i.e. cathodic and anodic to get polarization resistance, R_p. Tafel slopes were obtained by polarizing ±200 mV vs. OCP. From this slope, Tafel constant, B was determined and subsequently corrosion rate (CR) was calculated. The current corresponding to each potential was recorded and displayed on the monitor continuously.

3.2. Open circuit potential studies

For OCP measurements, each concrete test specimen was partially immersed in 5% NaCl and seawater and potential readings were obtained by placing a SCE firmly on concrete specimen. One of the two terminals of a digital voltmeter was connected to the SCE, and the other was connected to the exposed part of the reinforced steel bars to make a complete electrical circuit. OCP readings were taken of six specimens at one day interval for about a month followed by monthly/bimonthly/quarterly periods up to a total immersion period of 26 months. All the experiments were performed under free corrosion potential conditions and at ambient temperature.

3.3. Immersion tests

The laboratory immersion tests were carried out at ambient temperature and open atmospheric conditions. Concrete specimens were immersed vertically in 5% NaCl solution and seawater. The composition of the Gulf seawater is given in Table 1. In these media, specimens were dipped only 75% and 25% of the area remain exposed to air. NaCl solution or seawater were regularly replenished by adding required amount of distilled water to maintain the level in the container. Three specimens of each of the two coatings and without coating were taken out after immersion periods of 6, 12 and 24 months.

A batch of specimens comprising of specimens each from two coatings and without coating were installed at the sea coast near the intake of Al-Jubail plant to study the effect in tidal zone. The specimens were fixed in the special panel and then caged in a net in order to prevent the carry over of the specimens by the waves especially during high tide or under high wind conditions. The concrete specimens of each coating were taken out after an immersion period of 6, 12 and 24 months.

Table 1
Composition of Arabian Gulf seawater at Al-Jubail

Constituents	Arabian Gulf seawater, Al-Jubail
Cations (ppm)	
Sodium, Na^+	13440
Potassium, K^+	483
Calcium, Ca^{2+}	508
Magnesium, Mg^{2+}	1618
Copper, Cu^{2+}	0.004
Iron, Fe^{3+}	0.008
Strontium, Sr^{2+}	1
Boron, B^{3+}	3
Anions (ppm)	
Chloride, Cl^-	24090
Sulfate, SO_4^-	3384
Bicarbonate, HCO_3^-	130
Carbonate, CO_3^{2-}	–
Bromide Br^-	83
Fluoride, F^-	1
Silica, SiO_2	0.09
Other parameters	
Conductivity (μS/cm)	62800
PH	8.1
Dissolved oxygen (ppm)	7
Carbon dioxide (ppm)	2.1
Total suspended solids (ppm)	20
Total dissolved solids (ppm)	43800
Temperature range (°C)	18–33

4. Results and discussion

4.1. Electrochemical studies

4.1.1. Potentiodynamic polarization studies

The electrochemical parameters including polarization resistance (R_p), corrosion current (I_{corr}), CR, Tafel-C, Tafel-A and corrosion potential (E_{corr}) were computed from the potentiodynamic polarization experiments.

The immersion tests were of 26 months duration. Fig. 2 shows plots of time vs. corrosion parameters (CR, I_{corr} and R_p) for uncoated (control) specimens immersed in seawater. The corrosion current, I_{corr} increases with time till a maxima is observed at 9.3 months then there is a decrease in current value till 17.4 months when a minima is obtained, the current again increases up to 22.9 months when it drops down sharply up to 26 months. The alternate cycles of increase and decrease in corrosion current values can be attributed to breaking up of

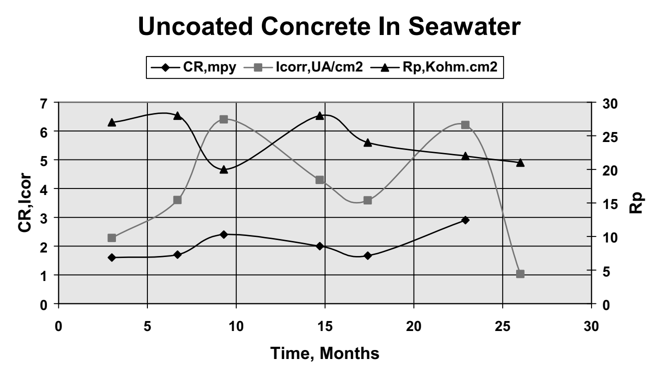

Fig. 2. Time vs. CR, I_{corr} and R_p plot for uncoated (controlled) samples in seawater.

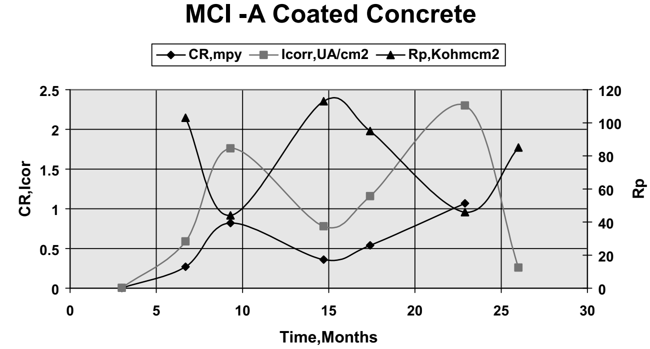

Fig. 3. Time vs. CR, I_{corr} and R_p plot for MCI-A coated concrete samples in seawater.

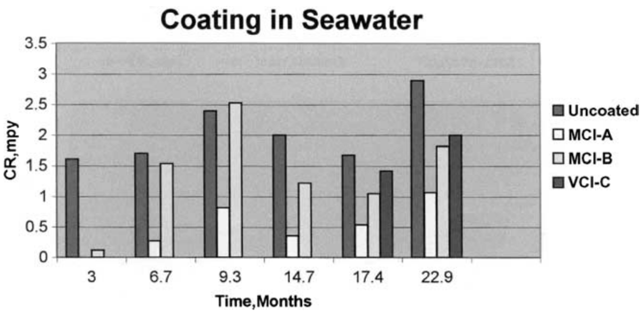

Fig. 4. Bar diagram representing CR for different coatings immersed in seawater for various periods of time.

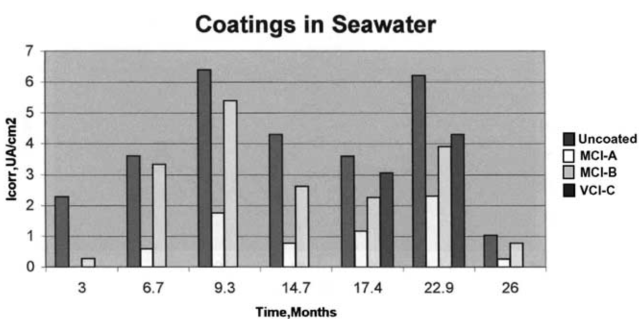

Fig. 5. Bar diagram representing I_{corr} for different coatings immersed in seawater for various periods of time.

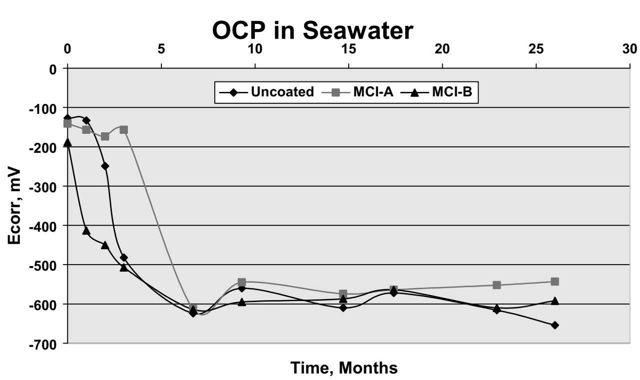

Fig. 6. OCP vs. immersion time plot for uncoated and coated concrete samples in seawater.

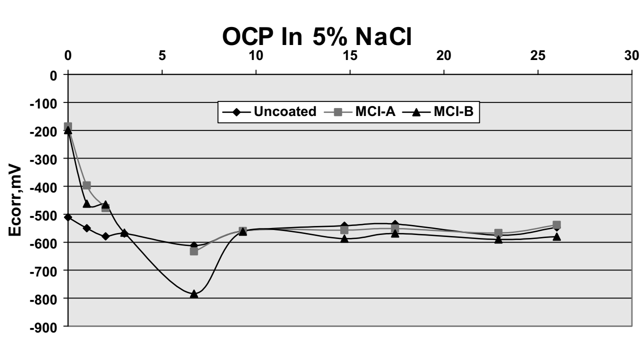

Fig. 7. OCP vs. immersion time plot for uncoated and coated concrete samples in 5% NaCl.

Fig. 8. Rebars in concrete under controlled condition in 5% NaCl solution. Immersion time: 19 months.

Fig. 9. Rebars in MCI-A coated concrete in 5% NaCl solution. Immersion time: 19 months.

Fig. 10. VCI-C coated rebarred concrete in seawater. Immersion time: 16 months.

Fig. 11. Rebars in MCI-B coated concrete in tidal zone. Immersion time: 16 months.

the protective film on rebar followed by passivation and then again depassivation due to the permeation of chloride through the pores of the concrete. Once the protective film breaks up, the bare metal is exposed to moisture and oxygen and consequently, oxide film will develop with time, however, continuous permeation of chloride again depassivates the film. Considering the electrochemical behavior of MCI-A—coated concrete specimens when compared to the control ones, i.e., uncoated; the CR and I_{corr} show identical behavior (Fig. 3) and R_p shows quite opposite behavior.

Fig. 4 represented by bar diagrams compares the corrosion rates of concrete under different coatings immersed in seawater for various periods of time. Following important points emerge from the analysis of bar diagram:

(1) There is an irregular relationship between corrosion rate and immersion time for uncoated and coated specimens in seawater.
(2) Corrosion rates of coated specimens are always lower than uncoated one (control).
(3) MCI-B has always higher corrosion rate and corrosion current density than MCI-A in seawater.
(4) Although the coating of VCI-C on rebar decreases the corrosion rates but it is not much effective while comparing to MCI-A and MCI-B.

Fig. 5 represents bar diagrams for CR of uncoated and coated concrete samples in 5% NaCl at different time intervals. The diagram shows that whilst the corrosion

Table 2
Condition of rebar after immersion of uncoated and coated samples In 5% Nacl

S. no.	Sample	Coating	Immersion time (months)	Visual observation*
1	N13	Uncoated	12	N
2	N14	Uncoated	12	N
3	N15	Uncoated	12	N
4	N16	Uncoated	19	N
5	N17	Uncoated	19	N
6	N18	Uncoated	19	N
7	B13	MCI-B	12	N
8	B14	MCI-B	12	VL
9	B15	MCI-B	12	VL
10	B16	MCI-B	19	VL
11	B17	MCI-B	19	N
12	B18	MCI-B	19	N
13	G13	MCI-A	12	VL
14	G14	MCI-A	12	N
15	G15	MCI-A	12	L
16	G16	MCI-A	19	N
17	G17	MCI-A	19	N
18	G18	MCI-A	19	N
19	V13	VCI-C coated rebar	9	N
20	V14	VCI-C coated rebar	9	VL
21	V15	VCI-C coated rebar	9	S
22	V16	VCI-C coated rebar	16	N
23	V17	VCI-C coated rebar	16	N
24	V18	VCI-C coated rebar	16	N

N: no, VL: very low, S: severe.
* Degree of corrosion.

rate of concrete are decreased on addition of MCI-A, the addition of MCI-B increases the corrosion rate considerably indicating the negative effect of MCI-B inhibitor. The presence of VCI-C rebar in concrete enhances the corrosion rate but the corrosion rate is slightly lower than MCI-B coated concrete specimen.

4.1.2. Open circuit potential measurements

Fig. 6 shows plots of immersion time vs. OCP for coated and uncoated concrete samples in seawater. The negative potential increases steeply in the first 6 months then it becomes almost constant with variation within ± 50 mV. MCI-A coated specimen exhibits more positive OCP values than MCI-B and controlled samples. The controlled sample appears to be more noble than MCI-B sample.

Fig. 7 shows plots of immersion time vs. OCP for coated and uncoated concrete samples in 5% NaCl solution. The control specimens do not show much variation in potential as compared to MCI-A and MCI-B though the OCP values are more negative. MCI-A has more positive OCP values than MCI-B. After more than 3 months, the OCP values remain constant yet there are only small variations within ± 20 mV. A large variation in potential to the negative side signifies rapid corrosion in the first 3 months of immersion, where as a constant potential is indicative of the stable condition of the oxide film. However, small variation in OCP values point out the on set of a cycle of alternate breaking and formation of oxide film which is more explicitly exhibited by plots of time vs. corrosion parameters.

4.2. Destructive testing of rebarred concrete samples exposed to various environments

The uncoated concrete and MCI-coated concrete samples were exposed to different environments which include 5% NaCl, seawater and tidal zone for various time durations. After exposition in the medium, the concrete samples were taken out and broken in a tensile machine by applying an appropriate load. The rebars of the samples were examined visually and the extent of corrosion was assessed qualitatively.

Figs. 8–11 show some typical photographs of uncoated and coated concrete samples in different environments. Considering the condition of rebars of uncoated concrete samples after immersion in 5% NaCl (Fig. 8), the rebars of the uncoated samples show no corrosion during 12 and 19 months tests (Table 2). The rebars of concrete samples coated with MCI-B and im-

Table 3
Condition of rebar after immersion of uncoated and coated samples in seawater

S. no.	Sample	Coating	Immersion time (months)	Visual observation*
1	N19	Uncoated	12	N
2	N20	Uncoated	12	L
3	N21	Uncoated	12	L
4	N22	Uncoated	19	L
5	N23	Uncoated	19	N
6	B19	MCI-B	12	L
7	B20	MCI-B	12	L
8	B21	MCI-B	12	L
9	B22	MCI-B	19	L
10	B23	MCI-B	19	M
11	B24	MCI-B	19	N
12	G19	MCI-A	12	L
13	G20	MCI-A	12	N
14	G21	MCI-A	12	L
15	G22	MCI-A	19	N
16	G23	MCI-A	19	N
17	G24	MCI-A	19	N
18	V19	VCI-C coated rebar	10	S
19	V20	VCI-C coated rebar	10	M
20	V21	VCI-C coated rebar	10	M
21	V22	VCI-C coated rebar	16	M
22	V23	VCI-C coated rebar	16	M
23	V24	VCI-C coated rebar	16	S

N: no, L: low, M: medium, S: severe.
* Degree of corrosion.

mersed in 5% NaCl for 12 and 19 months show no or very little corrosion. Concrete samples coated with MCI-A and immersed in 5% NaCl for 12 and 19 months, respectively also exhibit low corrosion and in some cases no corrosion (Fig. 9).

VCI-C coated rebar containing concrete samples immersed in 5% NaCl in general show no corrosion but in one case severe corrosion (Sample: V15) and in other case moderate corrosion (Sample: V14) is observed.

Considering the corrosion of rebars in uncoated concrete samples in seawater for 12 and 19 months, respectively, there is evidence of low or no corrosion from the visual examination (Table 3). The MCI-B coated concrete specimens immersed in seawater for 12 and 19 months show little or no corrosion in all the samples except one which exhibits some corrosion. MCI-A coated concrete samples in seawater show similar behavior as that found in case of MCI-B samples. The visual examination of the samples indicates no or marginal corrosion. The VCI-C coated rebar concrete samples in seawater show moderate to severe corrosion which is opposite to the behavior observed in 5% NaCl (Fig. 10).

The study of the corrosion behavior for rebars in uncoated and coated samples in tidal zone showed that majority of the samples have no or marginal corrosion but a few samples were found severely or moderately corroded after exposing to 12 or 21 months (Table 4). Surprisingly, MCI-B or MCI-A coated specimens in tidal zone show moderate corrosion after 12 months exposure but longer period (21 months) exposure tests show little evidence of corrosion barring a few cases which exhibit appreciable corrosion (Fig. 11). Concrete samples containing VCI-C coated rebar after exposure in tidal zone for 6 months show low corrosion but in samples exposed for longer durations (15 months), 3 out of 5 show low corrosion, one has low to medium corrosion and another one shows medium to severe corrosion.

Table 4
Condition of rebar after immersion of uncoated and coated samples in tidal zone

S. no.	Sample	Coating	Immersion time (months)	Visual observation*
1	N25	Uncoated	12	N
2	N26	Uncoated	12	M
3	N27	Uncoated	12	N
4	N28	Uncoated	21	L
5	N29	Uncoated	21	M
6	N30	Uncoated	21	N
7	N31	Uncoated	21	VL
8	N32	Uncoated	21	L
9	B25	MCI-B	12	S
10	B26	MCI-B	12	S
11	B27	MCI-B	12	VL
12	B28	MCI-B	21	VL
13	B29	MCI-B	21	VL
14	B30	MCI-B	21	L
15	G25	MCI-A	12	M
16	G26	MCI-A	12	M
17	G27	MCI-A	12	S
18	G28	MCI-A	21	S
19	G29	MCI-A	21	VL
20	G30	MCI-A	21	VL
21	V25	VCI-C coated rebar	6	L
22	V26	VCI-C coated rebar	6	M
23	V27	VCI-C coated rebar	6	M
24	V28	VCI-C coated rebar	15	N
25	V29	VCI-C coated rebar	15	L
26	V30	VCI-C coated rebar	15	N
27	V31	VCI-C coated rebar	15	N
28	V32	VCI-C coated rebar	15	M

N: no, L: low, VL: very low, M: moderate, S: severe.
* Degree of corrosion.

5. Conclusions

1. The results of electrochemical polarization (potentiodynamic) studies indicate that corrosion rates of MCI-A and MCI-B coated concrete samples are always lower than uncoated one (control) in seawater.
2. MCI-B coated concrete samples have invariably higher corrosion rates and corrosion current densities than MCI-A in seawater or 5% NaCl.
3. In seawater, I_{corr} decreases on addition of MCI-A or MCI-B but its decrease is very significant in presence of MCI-A.
4. In seawater, although the coating of VCI-C on rebar decreases the corrosion rates of concrete but it is much less effective while comparing with MCI-A and MCI-B.
5. The maxima and minima in R_p curves of uncoated and coated concrete samples invariably correspond to minima and maxima of I_{corr} and CR curves.
6. The CR of uncoated concrete in seawater are much higher than in 5% NaCl and E_{corr} in seawater is much more negative than in 5% NaCl indicating greater tendency of concrete to corrode in seawater.
7. In seawater, MCI-A and MCI-B coated samples have much higher positive OCP than control samples.
8. Destructive testing of uncoated (control) and coated samples exposed to various environments show the condition of rebar as follows:
   (a) In seawater, control, MCI-A and MCI-B coated samples show very little or no corrosion but VCI-C coated show medium to severe corrosion.
   (b) In 5% NaCl, control, MCI-A, MCI-B coated samples and VCI-C coated rebarred samples show very little corrosion.
   (c) In tidal zone, uncoated concrete shows varying degree of corrosion but normally small at low exposure time which enhances slightly with increasing exposure time. MCI-A or MCI-B coated and VCI-C coated rebars in concrete show in general little corrosion but in a few samples medium to severe corrosion was noted.

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