



Evaluation of a composite corrosion-inhibiting admixture and its performance in concrete under macrocell corrosion conditions

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Abstract

The objective of this present investigation is to design a composite corrosion-inhibiting admixture system comprising of both mineral and chemical admixtures and to evaluate its performance in concrete under macrocell corrosion conditions. The newly designed corrosion-inhibiting admixture system performed very well in chloride-contaminated concrete. Steel embedded in ordinary Portland cement suffered severe corrosion. In concrete incorporating the designed admixture system, steel showed a 10-fold decrease in corrosion rate of steel embedded in concrete under accelerated macrocell corrosion conditions. The compressive strength of mortars was not affected by adding the designed admixture system. © 2001 Elsevier Science Ltd. All rights reserved.

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1. Introduction

In recent years the use of various chemical and mineral admixtures in making high-performance concrete has increased significantly [1,2]. There is not enough information available on corrosion-inhibiting admixtures for steel embedded in concrete. Corrosion-inhibiting admixtures are mainly used in concrete exposed to seawater or to varying degrees of exposure to aggressive chemical environment. The use of different classes of corrosion-inhibiting admixtures in concrete have been reviewed by various authors [3–7]. Earlier studies looked at numerous corrosion inhibition admixtures with the most attention focused on sodium nitrite, potassium chromate, sodium benzoate and stannous chloride.

El-Jazairi et al. [8] examined the mechanical properties of mortars produced with sodium nitrite, potassium chromate, sodium benzoate and calcium chloride. They found a marked decrease in compressive strength as high as 20% to 40%, when the corrosion-inhibiting admixtures were added to concrete. In contrast, calcium chloride increased the

compressive strength, but the tensile strengths were adversely affected by the addition of sodium nitrite and sodium benzoate. Among all, only sodium nitrite inhibited the corrosion of steel embedded in concrete in the presence of chloride environments. They concluded that corrosion was uniform with sodium benzoate and pitting occurred with sodium nitrite.

Collepardi, Cigna et al. and Nurnberger and Beul [9–11] cautioned about the possibility of accelerated pitting of steel reinforcement in the presence of chloride when insufficient nitrite “under dosage” is present in concrete and expressed reservations with regard to the possible migration and leaching out of nitrite from concrete.

Sodium nitrite, however, suffers two disadvantages, one affecting reduction of strength and the other is the risk of the alkali–aggregate reaction which can be made worse by the addition of sodium nitrite [12,13].

Recently Monticelli et al. [14] studied more than 30 compounds as corrosion inhibitors for concrete application. Hansson et al. [15] also studied the principles of corrosion inhibitors in concrete.

Calcium nitrite meets ASTM C494 specifications as a concrete accelerator [8,16]. Calcium nitrite-based admixture provides a simple and cost effective corrosion protection

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system to the reinforced concrete even in small additions. But calcium nitrite is not indigenously commercialized in India. Only imported products are in large-scale commercial use.

The present investigation is to design a newer composite corrosion-inhibiting admixture system without affecting the strength properties and also to increase the corrosion resistance of steel embedded in concrete and the same is evaluated for its corrosion performance under macrocell corrosion conditions.

2. Materials and methods

2.1. Materials used

Ordinary Portland cement	Conforming to IS-456-2000
Graded coarse aggregates	Locally available aggregate conforming to graded aggregates of normal size greater than 4.75 mm and less than 10 mm of IS-456-2000
Graded fine aggregates	Local clean river sand (fineness modulus of medium sand equal to 2.6) conforming to grading Zone III of IS-383-1970 was used as fine aggregate.

2.2. Composition of mix design used

The mix design used for casting was as follows: 1:3:4.5 (w/c=0.6)

Constituents	Quantity used (kg/m ³)
Ordinary Portland cement	285
Fly ash	95
Coarse aggregates	1140
Fine aggregates	1710

2.3. Preparation of rectangular concrete specimens

A rectangular concrete specimen of size 279 × 152 × 114 mm was designed as per ASTM G 109-92 for macrocell corrosion studies. Mild steel cylindrical rod with the following properties:

OMS UTS (MPa)	380–420
Yield stress (MPa)	235–260
Elongation	20–23%

and of size 10 mm diameter, 300 mm length were used as both anode and cathodes in the same concrete. Initially the

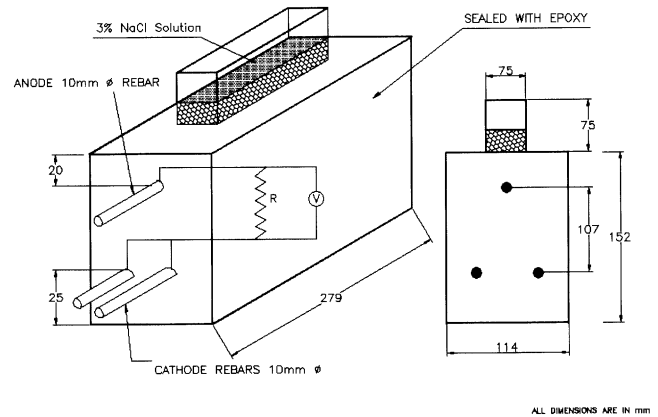


Fig. 1. Schematic view of macrocell specimen.

mild steel cylindrical rods were cleaned in hydrochloric acid, degreased with acetone and washed with double-distilled water. The top mat of the rebar acts as anode and the bottom mat of rebars acts as cathode. The anode to cathode ratio was maintained as 1:2 in order to induce accelerated corrosion. The configuration of macrocell specimen used is given in Fig. 1. In both the anode and cathodes, exposed length was 220 mm. The remaining length was used for taking electrical connections and properly insulating from the aggressive environment.

Concrete specimens were prepared using 1:3:4.5 mix with a w/c ratio of 0.6. During casting, AR grade corrosion-inhibiting admixtures were added for uniform distribution. The specimens were mechanically vibrated. After 24 h of setting, the specimens were demolded and cured in double-distilled water for 28 days. Then, all the concrete specimens were subjected to 3% NaCl wetting cycle immediately after curing. One alternate wetting and drying cycle consists of 15 days wetting with 3% NaCl solutions and 15 days drying. Measurements were carried out during wetting cycles as macrocell current showed maximum magnitude due to the low resistivity of concrete. All the concrete specimens were subjected to five complete cycles of test period.

2.4. Corrosion-inhibiting admixture system

The different systems studied were as follows:

Ordinary Portland cement (100%)	OPC
OPC + Fly ash (75%:25%)	FA
OPC + FA + sodium hydroxide (1%)	A
OPC + FA + sodium hydroxide (1%) + sodium citrate (1%)	B
OPC + FA + sodium hydroxide (1%) + sodium citrate (1%) + sodium stannate (1%)	C
OPC + FA + sodium hydroxide (1%) + sodium citrate (1%) + sodium stannate (1%) + calcium oxide (0.5%)	D

2.5. Methods

2.5.1. Potential vs. number of cycles

The open circuit potential of mild steel anode was monitored for every cycle under alternate wetting and drying conditions using saturated calomel electrode (SCE) as reference electrode.

2.5.2. Macrocell current vs. number of cycles

Macrocell current flow between anode and cathode was measured using a high-impedance voltmeter. The top mat and bottom mat rebars were connected by a 100- Ω resistor and macrocell current was obtained from the relation $I = V/100$. Current was monitored once in every cycle until the average macrocell current of the control specimens is 10 μ A or greater. The tests continued up to five complete cycles of exposure (150 days) to ensure the presence of sufficient corrosion for visual examination.

2.5.3. Total integrated current vs. number of cycles

The total integrated current for each system was calculated as per ASTM G 109-92 (Eq. 1).

$$TC_j = TC_{j-1} + [(t_j - t_{j-1}) \times (i_j + i_{j-1}) / 2] \quad (1)$$

where TC = total corrosion (coulombs); t_j = time (seconds) at which measurements of the macrocell current is carried out; i_j = macrocell current (amps) at time t_j .

2.5.4. Effect of admixture on compressive strength

Compressive strength of cubes of size 100 \times 100 \times 100 mm containing ordinary Portland cement (control) and specimens containing various corrosion-inhibiting admixtures were tested in an AIMIL compression testing machine having a capacity of 2000 kN as per IS 456-2000. This test was carried out in triplicate specimens.

Mortar (1:3) specimens with water to cement ratio of 0.5 containing various corrosion-inhibiting admixtures were cured for 28 days in double-distilled water and then tested.

2.5.5. Qualitative and quantitative estimation of corrosion

At the end of the exposure period, the concrete specimens were split open and the anode (rebar) was rated for rusted area and expressed in terms of percentage of area rusted. The corrosion rate of mild steel anodes embedded in control (OPC) specimen and in various corrosion-inhibiting admixtures were determined by gravimetric weight loss method and expressed in millimeters per year (mmpy).

2.5.6. Chemical analysis for alkalinity and free chloride

The core samples collected near the anode were crushed mechanically and powdered. Then 100 gm of powdered sample was shaken with 200 ml of double-distilled water in a conical flask using Microid flask shaker for 1 h. The extract was then filtered through a

Whatman filter paper No. 42. The extract prepared from the powdered sample was then analyzed for alkalinity and the free chloride contents as per the standard procedures [17].

A 50-cc filtered solution was put in a 100-ml beaker and the alkalinity of the sample was measured in terms of pH using a standard calibrated pH meter.

A 20-cc filtered solution was taken and the free chloride was estimated by standard silver nitrate using potassium chromate as an indicator. The amount of chloride present was expressed in terms of parts per million (ppm) on the basis of weight of sample taken for analysis.

3. Results and discussion

3.1. Potential vs. number of cycles

The electrochemical characteristics of half-cell potentials measured periodically against a SCE with time are shown in Fig. 2. From the figure it was inferred that initially up to one cycle of exposure for all the systems showed potential values ranging from 0 to -300 mV vs. SCE which reflected the passive condition of embedded steel anode. After that, steel embedded in control specimens showed a very high negative potential of -400 mV vs. SCE at two cycles of exposure whereas other systems namely A, B, C, and D showed potential values ranging from -150 to -300 mV vs. SCE. This interesting observation was due to the perfect passive condition of the steel anodes even after two cycles of exposure. After five cycles of exposure, steel anode embedded in concrete without inhibiting admixture showed a very high negative potential of -550 mV vs. SCE. This indicated the severe corrosion of the anode. But the steel anodes embedded in various admixture systems showed less negative potential. System D showed only -350 mV vs. SCE even after five cycles of exposure. In System D perfect passive condition was observed due to the inhibiting and complexing ions, such as citrate and stannate, which were more responsible for forming a stable com-

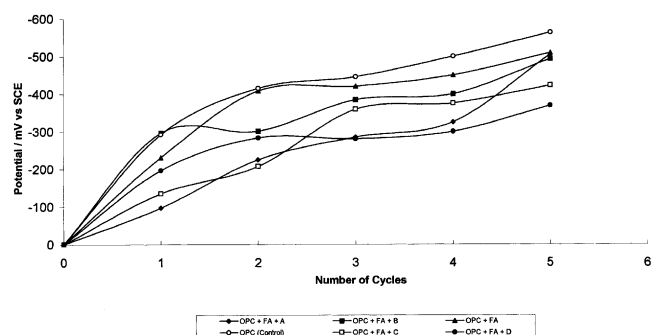


Fig. 2. Potential vs. number of cycles for different systems under macrocell conditions.

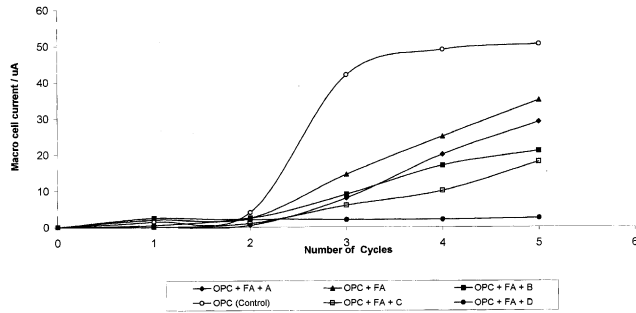


Fig. 3. Macrocell current vs. number of cycles for different systems under macrocell conditions.

plex and calcium oxide maintains the perfect alkalinity near the steel surface. The possibility of complex formation leads to some of the attacking anions being rendered inactive. Therefore, the combined effect of all these ions maintains a perfect passivity on the steel surface even in the presence of higher concentrations of aggressive chloride ions.

At the end of exposure, the corrosion protection of steel embedded in concrete by the different systems based on potential vs. number of cycles follows the order:

$$D > C > B > A > FA > OPC.$$

3.2. Macrocell current vs. number of cycles

The macrocell current or galvanic current measured periodically with time are shown in Fig. 3. From the figure, it was observed that even after two cycles of exposure no significant current flowed between anode and cathodes in all the systems. After three cycles of exposure steel anode embedded in control showed a very high current in the order of 45 μA , whereas the steel anode embedded in admixture systems showed current in the order of 15 μA . A three-fold increase in current was observed for the control specimen. This observation clearly proved that in the case of admixture concretes the inhibition was due to the formation of an insoluble stable complex film through the process of chemisorption on the metal surface. The film integrity was also confirmed by potential vs. number of cycles behavior. At the end of the exposure period the reduction in macrocell current for the different systems follows the order:

$$D > C > B > A > FA > OPC.$$

Among these systems studied, System D showed negligible amount of macrocell current flow. This observation indicated that the presence of inhibitive ions like hydroxide, citrate, and stannate reacts with calcium present in the concrete and forms a stable complex layer on the steel anode. The better performance of System D can be explained as follows. The relative amounts of

chloride and complexing anions available at the reinforcing steel determine whether the ferrous ions react firstly with the chlorides or the complexing anions. In the case of steel anode embedded in OPC concrete, stimulators like chloride ions, which can occupy the defect position and react with ferrous ions, begin the corrosion process. Consequently, 50 μA current flow in the macrocell. On the other hand, in System D the steel initially with $\gamma\text{-Fe}_2\text{O}_3$ film was further blocked by inhibitive and complexing agents. Therefore, ferrous ions preferably react with complexing anions than with chloride ions. Consequently, a straight-line behavior was observed throughout the test period of five complete alternate wetting and drying cycles.

3.3. Total integrated current vs. number of cycles

The total integrated current calculated with time for various admixture systems are illustrated in Fig. 4. From the figure it was clearly indicated that as observed in macrocell current vs. number of cycles behavior, all the systems showed negligible amount of current flow up to two cycles of exposure. After three cycles of exposure under proposed test conditions steel anodes embedded in ordinary Portland cement showed 90 Coulombs whereas the steel anodes embedded in various admixture systems namely A, B, C, and D showed only below 50 Coulombs. At the end of the test period (after five cycles) steel anode embedded in ordinary Portland cement showed 325 Coulombs whereas the steel anodes embedded in various admixture systems showed a lesser current. As observed earlier, the reduction in the total integrated current for the different systems follows the order:

$$D > C > B > A > FA > OPC.$$

Even after five cycles of exposure System D showed negligible amount of current flow. This observation clearly proves that even in the presence of chlorides the admixture systems effectively reduce the corrosion of embedded steel in concrete.

The above results were in concordance with that observed in potential vs. number of cycles and macrocell current vs. number of cycles studies.

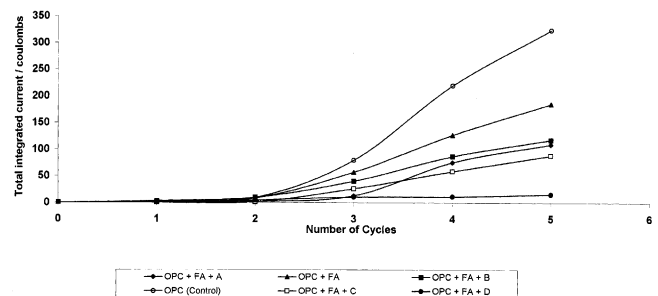


Fig. 4. Total integrated current vs. number of cycles for different systems under macrocell conditions.

Table 1
Qualitative and quantitative estimation of corrosion

System	Compressive strength (MPa)	Alkalinity (pH)	Free chloride contents (ppm)	Area rusted (%)	Corrosion rate (mmpy)	Durability factor
OPC	20.5±2	11.6	1500	80	0.229	–
OPC+FA	18.5±1.2	11.6	1560	5	0.154	1.50
A	21±1.5	12.0	1520	2	0.132	1.73
B	22±2.5	12.2	1540	2	0.098	2.34
C	23±2.0	12.2	1545	0.5	0.083	2.76
D	25.5±1.7	12.2	1510	0.5	0.029	7.90

3.4. Effect of admixtures on compressive strength

Compressive strength of 1:3 mortar prepared using $w/c=0.5$ after 28 days of curing are reported in Table 1. The average compressive strength for 100% OPC was 20.5 ± 2 MPa whereas that for various admixture mortars showed compressive strength ranging from 21 to 25 MPa. From this table it was concluded that the addition of admixtures did not affect the compressive strength of mortars. The important prerequisite for good admixture [18] systems is the ability to reduce the corrosion of steel embedded in concrete in aggressive chloride environments and as well as not to affect the strength properties of concrete. In this aspect, System D performs better than other systems studied.

3.5. Qualitative and quantitative estimation of corrosion of steel

At the end of the test period the steel anodes embedded in ordinary Portland cement and in various admixture concretes were analyzed for qualitative and quantitative estimation of extent of corrosion. The visual observations and weight loss data are reported in Table 1.

The qualitative evaluation revealed that in 100% OPC concrete, steel showed 80% corroded zone. But in admixed concrete, steel showed only 2% corroded zone. Systems C and D showed negligible amount of corrosion even in the presence of aggressive chloride for the longer period.

The quantitative evaluation revealed that steel anode embedded in 100% OPC showed a corrosion rate of 0.229 mmpy, whereas steel anode embedded in various admixture concretes showed much less corrosion rate (Table 1). Actually, in the case of System D, a 10-fold decrease of corrosion rate was observed (0.029 mmpy). Among different systems studied, System D effectively enhanced the durability of steel embedded in concrete under aggressive macrocell corrosion conditions.

3.6. Alkalinity and free chloride contents

The results of core sample analysis are reported in Table 1. From this table it is observed that both ordinary Portland cement and OPC containing 25% fly ash showed a slight decrease in alkalinity (pH=11.6)

whereas all the admixed systems showed preservation of concrete alkalinity (pH=12.2) even after five cycles of alternate wetting and drying. This observation clearly proved that the alkalinity of concrete was not at all affected by adding admixtures. The preservation of alkalinity even in the presence of higher amounts of chlorides helped the steel anodes to maintain the perfect passive condition throughout the test period. The free chloride contents estimated were reported in Table 1. As the test condition was maintained uniformly, all the concrete cubes showed uniform penetration of chloride. The free chloride contents estimated remains the same in all the specimens, i.e. ranging from 1510 to 1560 ppm of chloride.

4. Conclusions

The following conclusions can be drawn from the present investigation:

1. Steel embedded in ordinary Portland cement suffered severe corrosion under macrocell conditions. However, admixed concrete improved the corrosion resistance properties of steel.
2. The alkalinity of concrete was not at all affected by adding the corrosion-inhibiting admixtures.
3. Admixture systems containing hydroxide, citrate, and stannate not only decreased the corrosion rate of steel embedded in concrete under accelerated corrosion conditions but also increased the compressive strength of mortars.
4. Admixture systems containing hydroxide, citrate, and stannate showed a 10-fold decrease in corrosion rate of steel embedded in concrete under accelerated macrocell corrosion conditions.
5. Citrate, stannate, and calcium oxide composite admixed systems effectively controlled the corrosion rate of steel embedded in concrete and enhanced the durability under macrocell conditions.

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