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Competitive role of inhibitive and aggressive ions in the corrosion of steel in concrete

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Abstract

The effect of various inhibitive ions (hydroxide, citrate, stannate) for the corrosion of steel in concrete was studied by weight loss measurements, chronopotential studies, anodic polarization technique and compressive strength tests. The salient features of the investigation were: in 100% OPC as well as in OPC + fly ash (3:1 ratio) extracts the passivity of steel was readily destroyed even by the presence of 10 000 ppm of chloride. However in 100% OPC and also in OPC + fly ash (3:1 ratio) extracts containing inhibitive and complexing agents like hydroxide, citrate and stannate, the passivity of steel was maintained even in the presence of 30 000 ppm of chloride. The addition of inhibitive ions like hydroxide, citrate and stannate not only decreased the corrosion rate of steel in simulated concrete environments but also increased the compressive strength of mortars. Citrates, stannates and CaO are effective inhibitors of the corrosion of steel in concrete.

1. Introduction

The corrosion of steel in concrete is influenced by various factors [1–5]. Among the factors, chloride induced corrosion plays a major role in decreasing the durability of concrete structures [6–10]. To counteract this corrosion problem various preventive measures have been reported [11–13].

In Portland cement concrete, competition between chloride and hydroxyl ions may result in corrosion of embedded steel if oxygen is available for cathodic reaction. Streicher [14] studied the competitive adsorption of aggressive chloride ions in the presence of inhibitive ions. The tolerable limit of chloride was found to increase with increase in the concentration of the inhibitor ions. For a constant concentration of the inhibitor the corrosion current varied with the concentration of the aggressive ion according to Equation 1:

$$\log i_{\mathrm{corr}} = a_1 + b_1 \log C_{\mathrm{agg}} \tag{1}$$

For a constant concentration of the aggressive ion the corrosion current varied with the concentration of the inhibitor as follows:

$$\log i_{\mathrm{corr}} = a_2 + b_2 \log C_{\mathrm{inh}} \tag{2}$$

The constants a_1, a_2, b_1 and b_2 indicate high adsorbability of inhibitors in forming a compact layer at the metal surface resisting the penetration of the small chloride ions. Studies were carried out for the critical concentration of inhibitor anions to counteract the corrosion induced by aggressive ions. Inhibitors such as nitrites, benzoates and phosphates were studied [15, 16]. Thangavel and Rengaswamy studied the effect of the Cl^-/OH^- ratio on the corrosion rate of steel in concrete [17] and outlined important factors to be considered in assessing the rate of corrosion of steel in concrete under field conditions. According to Treadaway and Russell both sodium nitrite and, to a greater extent, sodium benzoate seriously reduced the strength of the concrete and their use in large quantities as admixtures was questionable [18]. There is a lack of detail about practical implementation of inhibitors to counteract the aggressive chloride effect. The present investigation deals with systematic studies on the competitive role of specific inhibitors and complexing agents such as hydroxides, citrates, stannates and CaO in the presence of aggressive chlorides in controlling the corrosion rate of steel in concrete.

2. Experimental details

2.1. *Materials*

Mild steel cylindrical rod of OMS UTS 380–420 MPa and yield stress 235–260 MPa was used throughout this study. Mild steel cylindrical rod of size 6 cm long and 0.6 cm diameter was used for weight loss and open circuit potential measurements (o.c.p.). A cylindrical mild steel rod of the same diameter as above, with an exposed area of 5.65 cm^2, was used for polarization measurements. The electrode was polished, degreased and then cleaned with distilled water and dried. All solutions were prepared from LR grade sodium hydroxide and distilled water. The following inhibitors and complexing agents were used: Sodium citrate (Ranbaxy GR grade), sodium stannate (Loba Chemie GR grade) and calcium oxide of high purity grade (BDH). The calcium oxide was heated for a long time to decompose any calcium carbonate contained in the sample; it was then cooled and stored in a dessicator prior to use. Sodium chloride used was of LR grade (Fischer).

Ordinary Portland Cement (OPC) and fly ash (FA) were used; the compositions are given in Table 1.

Table 1. Composition of OPC and fly ash

Constituents	OPC/%	Fly ash/%
SiO_2	22.14	57.95
Fe_2O_3	3.35	11.70
Al_2O_3	9.93	15.50
CaO	60.68	9.50
MgO	1.30	3.00
Loss on ignition	2.60	2.35

2.2. *Methods*

2.2.1. *Preparation of cement extracts*

Ordinary Portland cement + fly ash (3:1 ratio) were mixed thoroughly. 100 g of total cement contents were dissolved in 200 ml of distilled water. The cement + water mixer was shaken mechanically for 1 h. The cement extract was then collected by filtration. All the experiments were carried out in cement extracts with various addition of chlorides (10 000, 20 000 and 30 000 ppm of Cl^-) and various inhibitors and complexing agents.

The systems studied were:

Sodium hydroxide (pH 12.7) (A)

Sodium hydroxide + Citrate (pH 12.5 to 13.0) (B)

Sodium hydroxide + Citrate
+ Stannate (pH 12.5 to 13.0) (C)

Sodium hydroxide + Citrate + Stannate
+ Calcium oxide (pH 12.5 to 13.0) (D)

2.2.2. *pH measurements*

The alkalinity of ordinary Portland cement – fly ash cement extracts and extracts containing various inhibitors and complexing agents in the presence of different concentration of chlorides were measured using a standard calibrated pH meter. The pH measurements were carried out, initially and subsequently up to 90 days of exposure. The initial pH and the pH after 90 days of exposure are given in Table 2.

2.2.3. *Determination of self-corrosion rate*

Weight loss measurements were performed as described earlier [19]. Triplicate test specimens, suspended from hooks on a glass rod, were introduced into a beaker containing 200 ml of the test solution of ordinary Portland cement – fly ash cement extracts (control) and extracts containing various inhibitors and complexing agents with different chloride concentrations. The weight loss experiment was carried out for 90 days for each system in different test solutions. All the tests were conducted at room temperature (31 ± 1 °C). At the end of each run, the specimens were removed, washed thoroughly with running water, rinsed with distilled water and dried. Corrosion rates were determined gravimetrically [20].

2.2.4. *Measurement of open circuit potential (o.c.p.)*

The o.c.p. of mild steel specimens in different test solutions were measured by dipping polished and degreased specimens in the respective solutions for about 30 min. During this time the o.c.p. values reached steady states. The steady-state potentials were measured with respect to a saturated calomel electrode (SCE) by means of a digital multimeter (HIL-2161) with very high input impedance. O.c.p. measurements were monitored up to 90 days of exposure in different test solutions.

2.2.5. *Anodic polarization*

Anodic polarization was carried out using a Wenking potentiostat. The working electrode was a cylindrical rod with an exposed area of 5.65 cm^2. Platinum foil of larger area and a saturated calomel electrode (SCE) served as the auxiliary and reference electrodes,

Table 2. Weight loss measurements for mild steel in OPC + FA extracts containing inhibitive and complexing agents with different concentrations of chloride (90 days exposure)

No.	System (concn. in ppm)	Initial pH	Weight loss/g	Weight gain/g	pH at the end of exposure
1	Plain extract	12.3	0.1243	–	10.1
2	Plain + 10 000 Cl^-		0.1670	–	
3	Plain + 20 000 Cl^-		0.2443	–	
4	Plain + 30 000 Cl^-		0.3023	–	
5	A + 10 000 Cl^-	12.7	–	0.0009	12.5
6	A + 20 000 Cl^-			0.0007	
7	A + 30 000 Cl^-			0.0006	
8	B + 10 000 Cl^-	12.5–13.0	–	0.0145	12.5
9	B + 20 000 Cl^-			0.0124	
10	B + 30 000 Cl^-			0.0110	
11	C + 10 000 Cl^-	12.5–13.0	–	0.0286	12.5
12	C + 20 000 Cl^-			0.0260	
13	C + 30 000 Cl^-			0.0235	
14	D + 10 000 Cl^-	12.5–13.0	–	0.0460	12.5
15	D + 20 000 Cl^-			0.0447	
16	D + 30 000 Cl^-			0.0423	

respectively. Anodic polarization was carried out for all the systems from −700 mV to +400 mV at 31 ± 1 °C.

2.2.6. *Compressive strength of mortars*

The compressive strengths of cubes of size 10 × 10 × 10 cm containing various inhibitors and complexing agents were tested in an AIMIL compression testing machine having a capacity of 2000 kN as per IS: 456–1978. The tests were carried out in triplicate. Mortar (1:3) specimens with water to cement ratio of 0.5, containing various inhibitors and complexing agents were cured for 28 days in tap water, and then tested. The average value of each set of tests was recorded.

3. Results and discussion

3.1. *pH measurements*

The pH values measured for plain cement and fly ash extracts and extracts containing chlorides and inhibitors are given in Table 2. The pH for plain extract was 12.3. After adding chlorides and inhibitors the initial pH ranged from 12.5 to 13.0. Even after 90 days of exposure the extracts containing chlorides and inhibitors maintained the same pH (12.5). On the other hand the pH value changed drastically, to 10.1 for plain cement extracts after 90 days.

3.2. *Determination of self-corrosion rate*

The weight loss data for mild steel in ordinary Portland cement + fly ash (OPC:FA = 3:1) extracts containing different concentration of aggressive ion (chloride) and various inhibitive ions and complexing agents are shown in Table 2. In plain extracts the weight loss was 0.12 g after 90 days. However, in the presence of chloride, the weight loss increased with increasing chloride concentration. The weight loss measured, actually doubled in the presence of 20 000 ppm of chloride (0.24 g). On the other hand in the presence of aggressive, as well as inhibitive ions, negligible weight loss was observed. Actually, weight gain was observed due to the maintaining of perfect passivity of steel even in the presence of aggressive ions (10 000, 20 000 and 30 000 ppm of chloride). The weight gain for the different systems follows the order D > C > B > A. Inhibitive ions like hydroxide, citrate, stannate react with calcium present in the cement extracts and form stable complex surface layers. The passive film integrity was tested as reported earlier [21]. The protective activity of inhibitors for steel in OPC + FA extracts was retained when specimens dipped in inhibited solutions were transferred into fresh extracts and 3% NaCl solutions without inhibitor. This clearly shows that the inhibition is 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 chronopotential studies. From the weight loss data it was found that, among all the systems studied, system D was more effective in reducing self corrosion of steel, even in the presence of 30 000 ppm Cl^-. Complex formation leads to some of the attacking anions being rendered inactive. Thus the combined effect of all the ions maintains perfect passivity on the steel surface, even in the presence of higher concentrations of aggressive ions.

3.3. *Chronopotential studies*

The chronopotential measurements carried out for mild steel in cement extracts containing different inhibitive and complexing agents and aggressive ions (30 000 ppm of chloride) are shown in Figure 1. The system containing inhibitive ions shifted the potential in the cathodic direction. In the presence of 30 000 ppm of chloride, even after three months of exposure, perfect passivity was maintained in all the systems. When any inhibitor is added to concrete the result is a mixed inhibitor because the OH^- ions in cement extracts can be considered to act as a mild anodic inhibitor. The resulting potentials were found to be in the range −700 mV to −800 mV vs SCE. But for extracts containing OPC + fly ash + 30 000 ppm of chloride, the potentials were found to be in the range −500 mV to −250 mV vs SCE. Corrosion accelerators like chloride ions, which can occupy the defect position (competitively with OH^- ions), may induce corrosion. This was also confirmed by weight loss measurements.

3.4. *Anodic polarization*

The results of anodic polarization tests for mild steel in cement extracts (OPC + fly ash + 30 000 ppm of chloride) containing different inhibitive ions are presented in the Figure 2. In the case of OPC + fly ash + 30 000 ppm of chloride, passivity is destroyed. As a result, large anodic currents in the range 10–100 mA cm^{-2} were measured. On the other hand for systems containing various inhibitive ions like hydroxide, stannate, citrate and calcium oxide, very low anodic currents in the range 0.1–1.0 mA cm^{-2} were measured. The systems B, C and D also show passive regions. A similar observation was reported by Preece et al. [22]. These results agree with the weight loss measurements and chronopotential studies.

3.5. *Compressive strength*

The compressive strength of mortars (1:3, W/c = 0.5, 28 days curing) containing different inhibitive ions are listed in Table 3. Compressive strength was not affected by the addition of different inhibitive ions. The addition of inhibitors like hydroxide, citrate and stannate increased the compressive strength of mortars. For 100% OPC the compressive strength was 20.5 MPa and for the system D the compressive strength was 25.5 MPa. These results indicate that the inhibitive ions not only

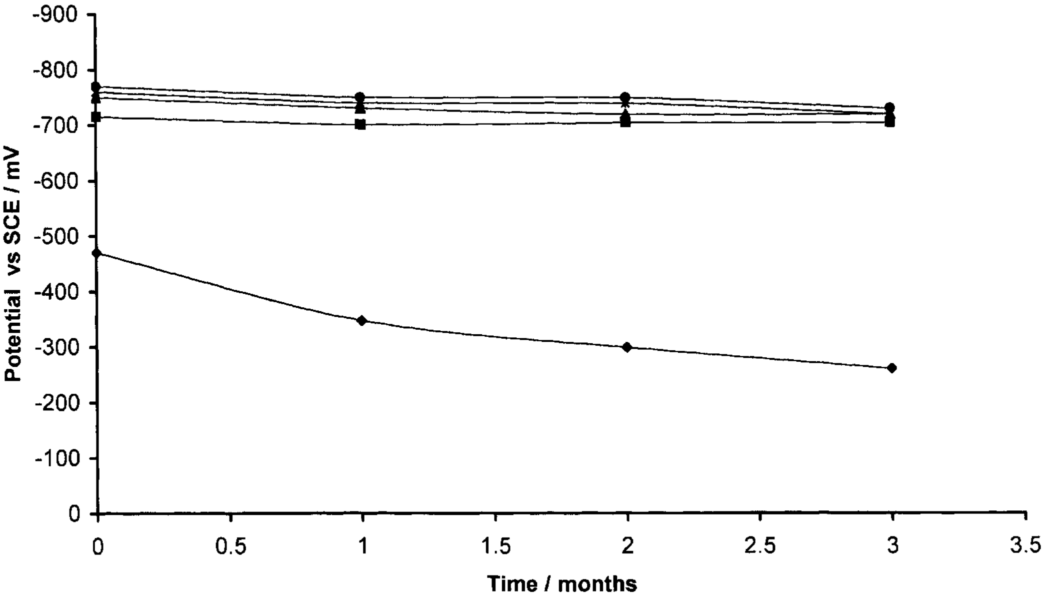

Fig. 1. Chronopotential behaviour of mild steel in OPC + FA extracts containing inhibitors and complexing agents with 30 000 ppm of Cl⁻. Key: (◆) Plain + 30 000 ppm Cl⁻; (■) A + 30 000 ppm Cl⁻; (▲) B + 30 000 ppm Cl⁻; (●) C + 30 000 ppm Cl⁻; (*) D + 30 000 ppm Cl⁻.

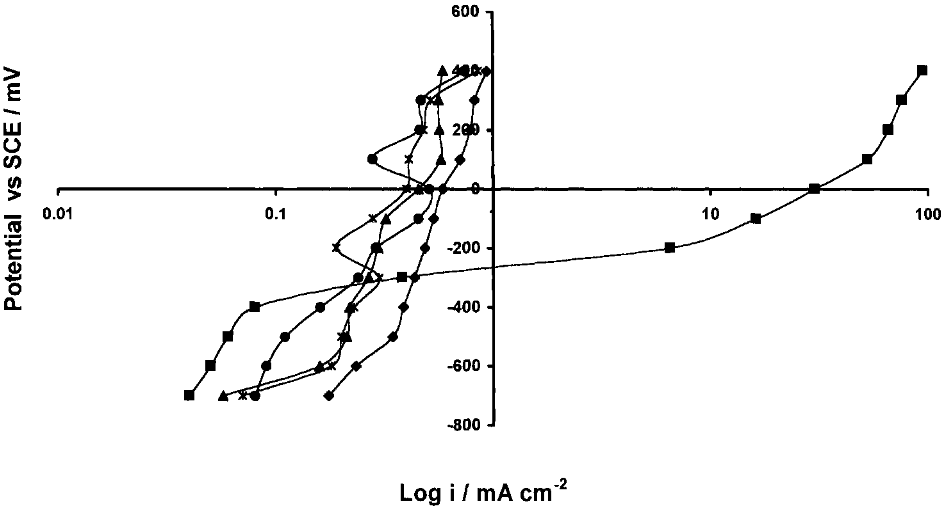

Fig. 2. Anodic polarization curves for mild steel in OPC + FA extracts containing inhibitors and complexing agents with 30 000 ppm of Cl⁻. Key: (■) Plain + 30 000 ppm Cl⁻; (◆) A + 30 000 ppm Cl⁻; (▲) B + 30 000 ppm Cl⁻; (●) C + 30 000 ppm Cl⁻; (*) D + 30 000 ppm Cl⁻.

Table 3. Compressive strength data for different systems of mortar at 28 days (1:3 mortar; W/C = 0.5)

No.	System	Compressive strength at 28 days/N mm^{-2}
1	100% OPC	20.5 ± 2
2	75% OPC + 25% FA	18.5 ± 1.2
3	75% OPC + 25% FA + A	21 ± 1.5
4	75% OPC + 25% FA + B	22 ± 2.5
5	75% OPC + 25% FA + C	23 ± 2.0
6	75% OPC + 25% FA + D	25.5 ± 1.7

decreased the corrosion rate of steel in concrete but also increased the compressive strength of mortars due to complex formation. A good inhibitor and complexing agent must have two important features: namely, (i) to reduce the self corrosion of steel to the maximum extent and (ii) not affect the strength properties of the mortar/concrete. In this aspect, system D was found to be more effective in controlling the corrosion of steel in concrete and also in not affecting the strength of mortar.

4. Conclusions

The result of these investigations have indicated:

(i) In 100% OPC and also in OPC + fly ash (3:1 ratio) extracts the passivity of steel was readily destroyed by the presence of chloride.

(ii) In 100% OPC and in OPC + fly ash (3:1 ratio) extracts containing inhibitive and complexing agents like hydroxide, citrate and stannate, the passivity of steel was maintained, even in the presence of 30 000 ppm of chloride.

(iii) The addition of inhibitive ions like hydroxide, citrate and stannate not only decreased the corrosion rate of steel in simulated concrete environments but also increased the compressive strength of mortars.

(iv) Citrates, stannates and CaO act as very effective inhibitors for controlling the rate of corrosion of steel in concrete.

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