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Fluoride induced corrosion of steel rebars in contact with alkaline solutions, cement slurry and concrete mortars

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Abstract

Corrosion behaviour of mild steel rebars has been studied in contact with 0.01 N NaOH, saturated lime water, cement slurry and embedded mortars having different concentrations of fluoride ions. Weight-loss, electrochemical DC cyclic polarisation and polarisation resistance, surface topographic and X-ray diffraction (XRD) techniques have been used to investigate the effects of fluoride ion on the corrosion behaviour of the material. Under all the conditions of the exposure it is observed that a low content of fluoride (≤ 25 ppm) in the corrodent has deleterious action on the performance of the steel, where as at its higher content (≥ 100 ppm) the ion has rather an inhibiting effect on corrosion rate. XRD studies of the corrosion product accumulated on the steel surface in the presence of fluoride ion indicate the predominance of magnetite oxide phase. Accelerating effect of the ion is observed to be due to depolarisation of cathodic reaction of the corrosion process. Observations show that in accelerating range of fluoride (≤ 25 ppm) it has almost double corrosive effect than noted for equal concentration of chloride ion. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Fluoride induced corrosion; Steel; Rebar corrosion; Corrosion due to chloride/fluoride; Cement slurry

1. Introduction

Out of various type of applications of steels, their use in concrete as reinforcement bars is perhaps in the largest proportion. Steels in contact of reinforcement cement

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concrete structures are expected to be safely protected from corrosive attack. This is owing to the alkalinity provided by the cement. The slurry of cement around the steel provides a pH of 12.5–13 which is considered to be very favourable condition for the formation of protective oxide layer on the steel surface. The protective condition, however, is disturbed once halides, sulphate, metal cations, moisture, oxygen and other corrosive gases reach near to the steel surface. Chloride is a well-known activator of uniform and localised corrosion. Similarly sulphate, although not directly involved in the corrosion process but helps in destabilising the concrete structures by the formation of voluminous ettringite phases and allows the penetration of oxygen and moisture to react with the reinforced steel surface.

Apart from chloride and sulphate ions which are well-known activators for corrosion of steel in reinforcement concrete structures, certain other anions are also encountered in soil, water and sand. Fluoride ion, although found in a small concentration in soil and water, is expected to affect the corrosion behaviour of reinforcement bars of steel. A detail literature survey has shown that the informations on the role of fluorides on corrosion of steel in alkaline environment or in cement slurry has been scarcely available. Fluoride ion is reported to have severe pitting attack on armco iron in alkaline environment where as in acidic solution, it induces uniform corrosion [1–4]. Further, this ion has more dangerous pitting attack at its lower concentrations than at higher concentrations [5]. Many researchers had reported that the ion at its higher concentrations, rather has an inhibiting effect on corrosion of carbon steels [5–12]. A lower level of fluoride causes an increasing effect on corrosion rate of steels with rise in temperature [13]. Zotikov et al. [5] have reported a decrease in corrosion rate of steel in contact of fluoride solution with passage of time. Macias and Escudero [14,15] observed that fluoride ions produce pitting attack on steel in alkaline media. However, the effect is reduced in lime saturated water due to the formation of CaF_2 salt which is sparingly ionisable. These authors have further claimed that due to the precipitation of fluoride ion as its calcium salt, the fluoride content is reduced below the threshold concentration required to cause pitting. Some other researchers had reported that fluoride ions either had no influence on passivity or improved the passivity of metals [16–18]. In contrast to this, Vasquez Moll et al. [19] and Mayer et al. [20] have reported that the presence of fluoride ions in corrosive aqueous solutions destroy the passivity and has an accelerating effect on pitting of mild steel. In a recent study conducted at the National Metallurgical Laboratory, Jamshedpur, India, it has been shown that the content of even 10 ppm of fluoride in cement slurry of water–cement ratio of 0.5 causes a pitting attack on reinforced bars [21]. This was confirmed by electrochemical as well as through direct microscopic examinations. These facts indicate that even in the presence of excess of Ca^{2+} , fluoride ions still remain active to cause the corrosion and pitting of steel rebars. It is probably due to the reason that even in the presence of excess of Ca^{2+} , calcium fluoride remains in soluble form to the extent of 15 ppm in solution [22]. In view of this a more detailed investigation on this aspect was felt necessary. The present study, therefore, was taken up to investigate the effect of low content of fluoride ion on corrosion of steel rebars by simulating the field conditions in the laboratory.

2. Experimental details

The steel samples used for experimental studies were in the form of bars of 16 mm diameter having ribs. The chemical compositions and mechanical properties of the steel bars are as follows:

Alloying elements as % of total weight:

$$C = 0.15, \quad Mn = 0.75, \quad S = 0.017, \quad P = 0.06, \quad Si = 0.21,$$

yield strength (YS) = 485 MPa, ultimate tensile strength (UTS) = 620 MPa and % elongation = 16.

The bars were thermomechanically treated (TMT) in the plant of M/S Tata Iron and Steel Company Ltd. of Jamshedpur, India, to have an outer ring of tempered martensitic structure of 2.5 mm breadth. The rest of the cross-section had ferrite–pearlite structure. For determining the mass-loss experienced by the steel samples in contact of corrosive electrolyte, the specimen in the form of bars were cut into the pieces of 100 mm length, pickled in inhibited 5% hydrochloric acid solution followed by wire buffing using soft wire brush mounted on an electrical motor. These samples were then polished using emery papers from rough to fine (600 grade) to provide a shining and smooth surface. All the samples were finally degreased using acetone, weighed and stored in a vacuum dessicator prior to exposing them in experimental solutions. The base electrolyte for the study was either 0.01 N NaOH, saturated lime water or water–cement (sulphate resisting portland cement) slurry of water to cement ratio (w/c) = 0.5. Fluoride and chloride ions were added in the base electrolyte as their sodium salts except in few cases where the effect of calcium ion was investigated. In this case calcium chloride was used to furnish chloride ions in the solution. The pH of cement slurry, 0.01 N NaOH and saturated lime solution was found to be between 12.5 and 13.0. These solutions were taken in view of the actual conditions of use of bars for reinforcement applications where the pH of the electrolyte of pore of concrete attains alkaline range (pH \simeq 12–13) and chloride, sulphate hydroxide and fluoride ions are actually found as their sodium and potassium compounds in the pore solution of the concrete. Calcium ions (Ca^{2+}) in the pore solution of concrete is derived from the lime used in manufacturing of cement. Chlorides are also added in cements as set accelerators/modifiers to improve the properties of the cast concrete. To study the effect of fluoride ion (F^-), sodium fluoride was used. Prior to the exposure of specimen, the sodium hydroxide and saturated lime water solutions were thoroughly aerated. The specimen were exposed in 250 ml plastic cylinders having air tight lids to avoid the diffusion of atmospheric gases in the solution. In all the cases, the ratio of the volume of corroding electrolyte to exposed metal surface area was maintained at 3 ml/cm². The weight-loss experiments were performed at room temperature (30 \pm 5 °C). The test solution in the cylinders were replaced with fresh aerated solution at an interval of seven days. After an exposure period of 42 days, the specimen were taken out from the test electrolytes, cleaned to remove corrosion products in Clarks solution (solution prepared by mixing 50 g/l SnCl₄ and 20 g/l Sb₂O₃ in concentrated hydrochloric acid (35% w/v) solution), rinsed with running tap water and kept in an oven at fixed temperature of 105 °C for 1 h. This was

necessary to ensure complete removal of any entrapped water/moisture from the pores of the corroded specimen. Before taking the final weight of the specimens, they were kept in dessicator for 18 h. All the experiments were performed in triplicate and an average value of the observed data was recorded. It was found that the average fluctuation in data was limited to below 2.5%. To avoid the contamination of the test electrolytes with other ions who might influence the corrosion property of the steel and mislead the findings, special attention was paid to use pure water free of ionic impurities, for the preparation of test electrolytes. To achieve it, doubly distilled water was used for making the test solutions. The ionic conductance of this water was observed $<1 \mu\text{s}$ whereas the chloride ion was in the ppb range only.

In addition to the above exposure tests of steel bar samples in direct contact of NaOH and saturated lime water solutions, some tests were also performed by embedding the bar samples in mortars prepared from cement + water + sand mixed in the proportion of 1:0.5:3 respectively. One set of mortar was prepared by mixing 0.25% chloride ion. The second set had 0.25% chloride + 0.0015% of fluoride ions whereas the third set had none of these ions. The percentage concentrations of ions (calculated as the weight of anions) were calculated on the basis of weight of cement taken for preparation of mortars. These concentrations were chosen as the analysis of concrete pores' solution in many areas having higher degree of salinity in water and soil had been found to fall in these ranges. Experiments in cement slurry were performed by preparing fresh slurry using double distilled water and sulphate resisting portland cement having the compositions (% by weight) as follows:

CaO = 65.5, MgO = 2.17, SO₃ = 1.23, SiO₂ = 21.52,
Fe₂O₃ = 4.95, Al₂O₃ = 4.85, Al₂O₃/Fe₂O₃ = 0.98,
C₃A(tricalcium aluminate) = 4.48,
loss on ignition = 1.56, acid insoluble residue = 1.72.

The mortars having steel bars were also cast by using the same cement. The surfaces of the bars before embedding in the mortars were prepared as stated above. The rebar samples of 160 mm length were cast in cylindrical mortars in such a way that a concrete cover of 16 mm thickness was available to the steel bar from all its sites. These mortars were demoulded after 24 h of casting and cured for 28 days in humidity chamber maintained at 95% RH and 35 °C temperature. After curing, they were exposed for 35 days in 3.5% sodium chloride solution. The embedded bars were then evaluated for change in their corrosion rate with passage of time by using DC polarisation resistance technique. The potential for polarisation was scanned at the rate of 0.015 mV/s. The potential values were scanned between ± 20 mV of open circuit potential of the embedded rebars. For the sake of simplicity, the values of anodic and cathodic Tafel slopes were taken as 0.12 V/decade in all the cases.

To investigate the effect of fluorides on generation and growth of pits, the specimen of 25 mm length were cut from the same lot of samples as taken for mass-loss studies. These samples were hot mounted in a resin resistant to alkali and water attack so that only one side of cross-sectional area was left uncovered. The cross-sectional area of the sample was grounded and polished on rough to fine grades of

silicon carbide emery papers followed by fine polishing on wheel using alumina powder of 0.1 μm size. This produced a completely scratch free surface when examined optically at 40 \times magnification. In middle of the polished surface, a sharp pit of 1 mm depth was generated using a sharp high speed steel driller having sharp tip. The specimen, after degreasing were exposed in the same electrolyte as described above for mass-loss studies. After an exposure period of 42 days, these samples were taken out and examined using scanning electron microscope (JEOL make).

Electrochemical polarisation studies of bar samples were performed in 0.01 N NaOH, saturated lime water and water cement slurry electrolytes. The specimen of 25 mm length and 16 mm diameter were mounted in resin as stated above. A hole of 5 mm diameter was drilled at the back side of the specimen to fit a copper rod of 7.5 cm length for taking the electrical connections. The experiments were performed in flex cell fitted with two graphite rods at two sides of the working electrode, which acted as auxiliary electrodes. The reference electrode was a saturated calomel electrode (SCE). A luggin capillary was used to provide electrolytic contact between the calomel electrode and electrochemical cell. The electrochemical studies were performed by using a Gamry potentiostat¹ supplied by M/S Gamry Instruments of USA. The scan rates for cyclic polarisation and DC polarisation resistance studies were fixed at 0.015 mV/s. The generated data were analysed by using CMS 105 software of M/S Gamry Instruments. The temperature of the test electrolytes was maintained through a NESLAB² water bath which was controlled with a sensor connected with the potentiostat. The temperature was maintained within an accuracy of ± 1 °C.

All the electrochemical studies were performed after exposing the specimen for 16 h in test electrolytes. This provided a reasonably stable open circuit potential and enabled the generation of reproducible data. The polarisation experiments were started from the cathodic region and went up to pre-determined potential/current at the interface. These studies were performed as per the recommendations of ASTM G59 and D-776 except that the maximum current allowed in cyclic polarisation was fixed at 5 mA/cm². This saved the samples suffering from severe attack and after repolishing, it was possible to use them for the other set of experiments.

The corrosion current density was calculated by using the equation

$$I_{\text{corr}} = \frac{1}{2.3R_p} (\beta_a \beta_c / \beta_a + \beta_c) = B/R_p, \quad (1)$$

where R_p is the polarisation resistance (measured by linear polarisation resistance technique) given by the equation $\{dE/dI_{\text{appl}}\}_{t \rightarrow \infty, \Delta E \rightarrow 0}$. These conditions were met by using very slow scan rate of potential (0.015 mV/s) and restricting the measurement between ± 20 mV of E_{corr} . β_a and β_c are the anodic and cathodic Tafel slopes respectively. These values were attempted to be derived from non-linear E vs $\log I_{\text{appl}}$ curves obtained within ± 0.1 V of E_{corr} . It was, however, noted that the values of 'B'

¹ A trade name of the instrument supplied by M/S Gamry Instruments, Warminster, USA.

² A trade name of the instrument supplied by M/S NESLAB of Newington, USA.

(which is equal to $1/2.3(\beta_a\beta_c/\beta_a + \beta_c)$) in all the cases were in the range of 0.0255–0.0267 V. For the sake of simplicity, the β_a and β_c values, therefore, were taken equal to 0.12 V which produced the value of $B = 0.026$ V. This assumption had very little effect on the calculated values of corrosion rate.

3. Results

The steel reinforcement bars during their service life, are expected to come in contact of aggressive ions under the following circumstances:

- (a) during the preparation of the concrete mixture where ions as contaminants in water/sand/gravel may reach at the surface of rebars and influence the corrosion rate;
- (b) chemicals used for making the special grades of cement such as quick setting and low energy cements where calcium chloride and fluorides are respectively added in the cement and;
- (c) as a result of the diffusion of aggressive ions through the pores of the concrete during service life of the structures.

In order to meet these three conditions, the following studies simulating the above conditions were performed.

For conditions (a) and (b): In this condition, aggressive ions come in contact of steel bars at the stage of making of the concrete slurry. To study the effect of the ions at this stage, the following set of experiments were performed:

- (i) corrosion behaviour of the steel bar in cement slurry (water/cement ratio = 0.5) having different concentrations of fluoride ions. This provides an idea about the role of ions on onset of corrosion prior to complete setting of the concrete;
- (ii) change in corrosion rate of the rebars embedded in mortars having water:cement:sand ratio of 0.5:1:3 and blended with different anions.

Since it was not possible to record appreciable changes in weight of bar samples during the short duration of tests under the above conditions, the studies were performed using electrochemical techniques only. In view of the earlier reports [14,15] where higher concentrations of fluoride ions are reported to have inhibitive effect on corrosion behaviour of steel in electrolytes having excess of Ca^{2+} , it was thought prudent to have first investigated the role of different concentrations of fluoride ion on corrosion rate of steel in lime saturated solution. The corrosion rates were determined by using DC polarisation resistance technique and the test conditions were maintained as stated in experimental part of this paper. The results are plotted in Fig. 1. It is evident from this figure that the corrosion rate of the steel initially increases up to 15 ppm of fluoride ion in the solution. Above this concentration, a gradual fall in corrosion rate with increase in its concentration is recorded. The corrosion potential, on the other hand, is observed to increase (more anodic)

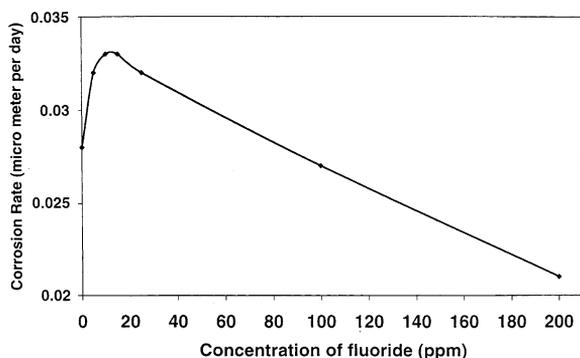


Fig. 1. Variation in corrosion rate of steel with increase in concentration of fluoride ion added in saturated lime water (corrosion rates were determined by polarisation resistance technique after exposing the specimen for 16 h in the test electrolyte).

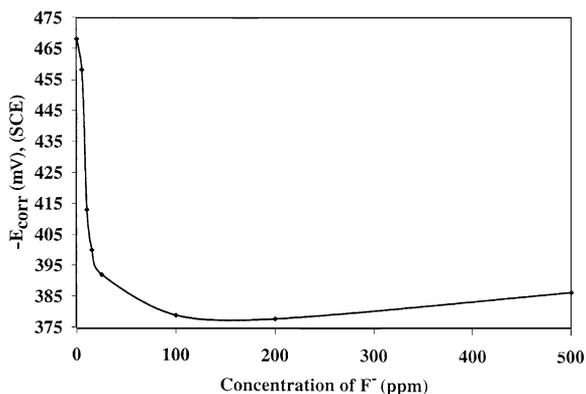


Fig. 2. Variation in corrosion potential (E_{corr}) of the steel sample with increase in fluoride content in saturated lime water (E_{corr} determined after exposing specimen for 16 h).

monotonically with increase in the concentration of the ion (Fig. 2). These observations indicate that the low content of fluoride (≤ 15 ppm) in lime saturated water solution has an acceleration effect on corrosion by depolarisation of the cathodic reaction whereas at its higher concentrations (≥ 15 ppm), the anodic reaction is polarised to bring down the corrosion rate of the steel. Since 15 ppm of fluoride ion was a critical value below which it had an accelerating effect on corrosion of steel, the further studies were mostly limited to this concentration only.

The results for the effect of fluoride ion on cyclic polarisation diagram for the steel bar in water–cement slurry having different ions are shown in Fig. 3. It is evident from this figure that the fluoride ion has no effect on trans-passive potential (E_t) of the steel. In the absence and the presence of fluoride ion, the increase in current density takes place practically at the same potential (0.58 V (SCE)). The cyclic polarisation curve for pure cement slurry having no contaminant, not only retraces the

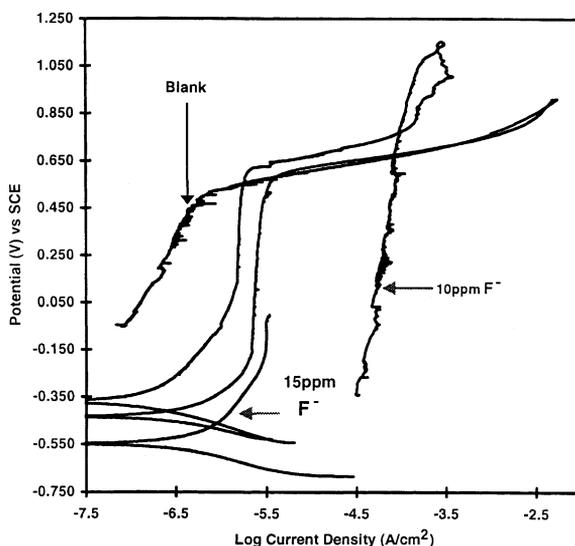


Fig. 3. Cyclic polarisation of the steel in cement–water slurry ($w/c = 0.5$) having different concentrations of fluoride ions.

trans-passive zone of the curve during the backscanning but also produces a lower passive current density. This indicates that the passive film on the steel surface during forward scanning is strengthened and this produces low passive dissolution current. In the presence of fluoride ions, however, the trans-passive zone of the curve generated during the forward scanning do not retraces at all on backscanning even up to the corrosion potential of the steel. The passive dissolution current density is observed to increase with increase in concentration of fluoride ion in the slurry. The corrosion rates evaluated by the Tafel extrapolation of anodic and cathodic polarisation plots in the vicinity of corrosion potential (± 120 mV of corrosion potential) (Table 1) show that the addition of fluoride ion in water–cement slurry has an accelerating effect on corrosion of the steel. This table further shows that the corrosion potential of the steel moves in nobler direction with increase in the concentration of the fluoride ion indicating a depolarising action on cathodic reaction. This is in conformity with the observations noted for the steel exposed in saturated lime water solution (Fig. 2).

The fluoride ion in combination of chloride ion has similar effect on the cyclic polarisation of the steel in contact of cement slurry (Fig. 4) except that very little effect on corrosion potential of the steel is recorded. Chloride ion on its own, however, shifts the potential in active direction (from -434 to -448 mV vs SCE) indicating a depolarisation effect on anodic reaction (Table 1).

Keeping in view the facts that the corrosion rate in combination of fluoride and chloride is accelerated to a considerable extent and corrosion potential is almost constant (-450 to -457 mV vs SCE) one can infer that these ions when present together in the slurry, result in simultaneous depolarising effect on anodic as well as

Table 1

Electrochemical parameters for mild steel in cement slurry ($w/c = 0.5$) in the presence of different ions

Sr. no.	Electrolyte	$-E_{\text{corr}}$ (mV) (SCE)	Corrosion rate ($\mu\text{m}/\text{day}$)
1	Slurry	434	0.0035
2	Slurry + 0.25% Cl^-	448	0.0389
3	2 + 0.0004% F^-	450	0.0227
4	2 + 0.0006% F^-	457	0.0529
5	2 + 0.0015% F^-	457	0.0529
6	Slurry + 3 ppm F^-	370	0.0056
7	Slurry + 10 ppm F^-	351	0.0056
8	Slurry + 15 ppm F^-	349	0.0122

The test specimen were exposed for 16 h in slurry prior to testing.

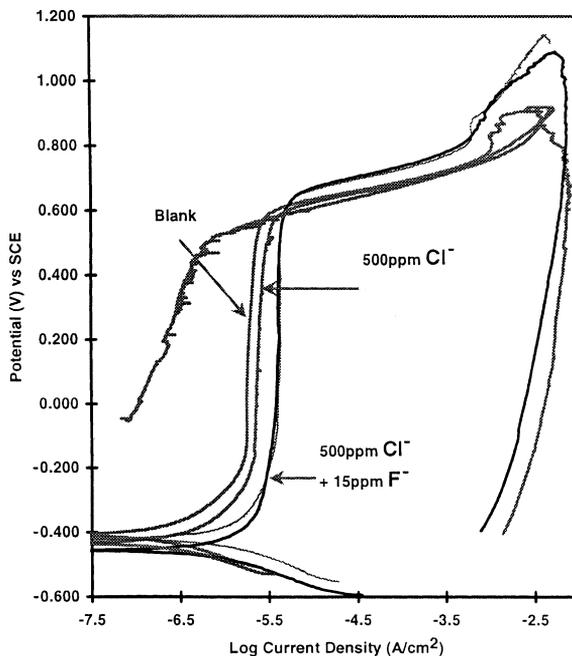


Fig. 4. Combined action of fluoride and chloride ions on cyclic polarisation of the steel in water-cement slurry ($w/c = 0.5$). Experiments were conducted after putting the test specimen in cement slurry for 16 h.

cathodic reactions. In order to confirm this observations under the actual embedded conditions of rebar in solid cast mortars, the studies were performed for embedded rebars in mortars having (i) no ions, (ii) blended with 0.25% of chloride and (iii) having 0.25% $\text{Cl}^- + 0.0015\%$ F^- ions. The data on corrosion rate, polarisation resistance and corrosion potential determined by DC polarisation technique are summarised in Table 2. The results of the table show that in the absence of any contaminant, the corrosion rate of the steel is extremely slow ($0.011 \mu\text{m}/\text{day}$). The

Table 2

Electrochemical parameters for mild steel bars embedded in mortars having different ions^a

Sr. no.	Mortars made by	R_p (Ωcm^2)	$-E_{\text{corr}}$ (mV)	Corrosion rate ($\mu\text{m}/\text{day}$)
1	W:C:S: :0.5:1:3	9.63×10^4	622	0.011
2	1 + 0.25% Cl^-	6.45×10^4	646	0.019
3	2 + 0.0015% F^-	3.41×10^4	647	0.025

% of Cl^- and F^- given in terms of weight by weight of ions to cement content in the mortars.

^a Data generated after exposing the mortars in test electrolytes for 30 days.

corrosion rate increases for the mortars having anions (for the mortar having 0.25% Cl^- , the corrosion rate is 0.019 $\mu\text{m}/\text{day}$ and for 0.25% Cl^- + 0.0015% F^- , the rate is 0.025 $\mu\text{m}/\text{day}$). The corrosion potentials after the addition of chloride ion shift considerably in active direction indicating that this ion depolarises the anodic reaction i.e. the dissolution of iron from the steel. However, in combination of chloride and fluoride, the shift is not appreciable which is exactly what we noted for the steel exposed in cement slurry (Table 1).

The above studies were performed keeping in view the circumstances under which the contaminant ions were present in the structure from the very beginning of the preparation of concrete mixture for the casting of structures. In this situation the calcium ion present in the cement in the form of lime plays very vital role. This ion is expected to react with sodium salts of fluoride ion to form sparingly soluble calcium fluoride [14,15].

Once the structure is cast the pore solution of the concrete is reported to have sodium and potassium hydroxides instead of calcium hydroxide [23–25]. Any diffusion of ions of chloride and fluoride, therefore, is expected to be present as their sodium or potassium salts. In this condition, the bar will be corroding in an electrolyte having alkaline pH (sodium/potassium hydroxide) and the above-mentioned ions. To investigate the role of these ions under such conditions, the studies were performed by exposing the steel bar samples directly to the solution of 0.01 N NaOH (pH = 12.6) in the presence and the absence of these ions. Weight-loss and electrochemical, both type of studies were performed to get authentic data on corrosion rates. The results of weight-loss data are incorporated in Table 3. The corrosion rate of the steel exposed in 0.01 N NaOH solution having different concentrations of fluoride ion in the presence of 0.25% of chloride ion derived from its sodium and calcium salts are incorporated in this table. It is evident from the results of the table that with increase in concentration of fluoride ion in the solution, the corrosion rate of the steel gradually increases. Another interesting observation recorded from this table is that the alkaline calcium chloride is about three to four times more corrosive than the alkaline sodium chloride under identical test conditions. Further, the severity of attack by fluoride ion with increase in its concentration is more in combination of NaCl than with CaCl_2 . At 1000 ppm of fluoride ion, for example, it has an accelerating effect of 66.6% for Na derived chloride where as for calcium derived chloride it is just 20.5%. This table further reveals that during the initial period of

Table 3

Corrosion rate evaluated by weight-loss method for the steel exposed in 0.01 N NaOH having different concentrations of fluoride ion in the absence and the presence of 0.25% of chloride ions derived from sodium and calcium chloride salts

Concentration of fluoride (ppm)	Corrosion rate ($\mu\text{m}/\text{day}$) in chloride solutions (derived from the salt of)					
	NaCl				CaCl ₂	
	Duration of exposure and corrosion rates ($\mu\text{m}/\text{day}$)				Duration of exposure = 42 days	
	10 days	42 days	% decrease in corrosion rate with passage of time	% increase in corrosion rate over controlled electrolyte	Corrosion rate ($\mu\text{m}/\text{day}$)	% increase in corrosion rate over controlled electrolyte
0	0.5519	0.0375	93.2	–	0.1426	–
10	0.5526	0.0522	90.5	38.9	0.1461	2.4
100	0.5498	0.0494	91.0	31.3	–	–
1000	0.5498	0.0626	86.6	66.6	0.1719	20.5

Experiments were performed at room temperature.

exposure (10 days), the corrosion rates are almost same at all the concentrations of the fluoride ion. At longer duration of exposure, however, the corrosion rate increases gradually with the concentration of fluoride ions. Further, the corrosion rate at longer duration of exposure decreases by one order of magnitude than that recorded for shorter duration of exposure. These observations indicate that although the anion has strong influence in accelerating the corrosion of steel in alkaline environment but the film formed on the steel surface in the presence of the ions is quite protective in nature.

The above results have clearly demonstrated that even the small concentration of fluoride ions in alkaline environment have an accelerating effect on corrosion of steel. In order to understand the role of fluoride in accelerating the corrosion, electrochemical studies were also performed by exposing the steel samples to 0.01 N NaOH in the absence and the presence of this ion. The cyclic polarisation plots for the steel in contact of this solutions having different concentrations of the fluoride ion are shown in Fig. 5. The figure shows that unlike water–cement slurry (Fig. 3) where the break-down in passivity of steel took place in anodic zone almost at the same potential for different concentrations of fluoride, the break-down potential of the steel in this case gradually decreases with the increase in the concentration of fluoride ions. At 100 ppm of fluoride ion, the passivity of the steel has completely disappeared and the anodic current exponentially increases with the increase in anodic potential starting from open circuit potential of the steel. This indicates that the steel loses its passivity completely in contact of sodium hydroxide solution having 100 ppm of fluoride ion. With gradual increase in fluoride ion concentration from 0 to 100 ppm the anodic branch of the curves are also shifted bodily in higher current density regions, indicating an acceleration of corrosion rate. A comparison of the curves of

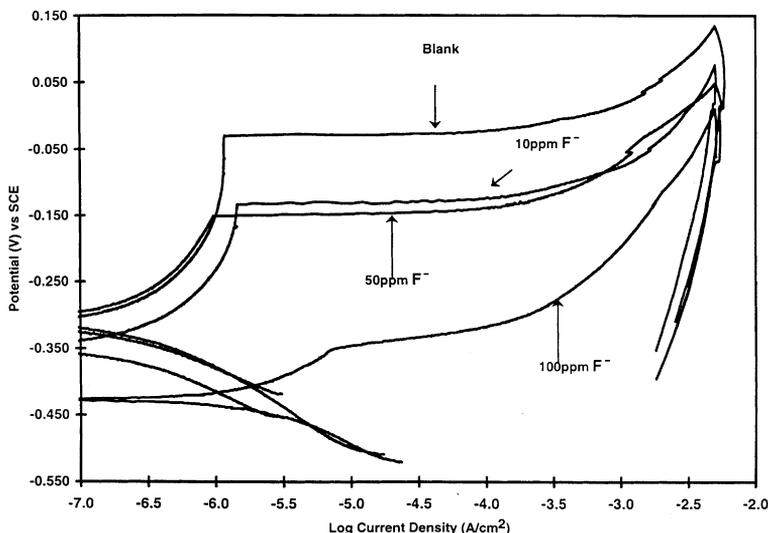


Fig. 5. Cyclic polarisation plots for mild steel exposed in 0.01 N NaOH having different concentrations of fluoride ions. Experiments were run after 1 h of exposure of specimen in test electrolytes.

Figs. 3 and 5 indicates that the presence of excess of Ca^{2+} in the electrolyte has a definite positive effect on control of fluoride induced corrosion of steel.

During the study of corrosion rate by weight-loss method, it was observed that the corrosion rate of the steel decreased with increase in exposure time (Table 3). It was thought, therefore, interesting to know what mechanism had played in bringing down the corrosion rate. To study this aspect, the coupons were exposed in the test electrolytes for 14 days and then cyclic polarisation studies were performed in the same solution without disturbing the electrodes. The plots are shown in Fig. 6. It is evident from this figure that the aggressive anions do not have any tendency to break-down the passivity of the steel even after raising the anodic potentials to quite a high value (more than $+0.750$ mV to E_{oc}). In contrast to this, the steel samples exposed in 0.01 N NaOH and polarised within 1 h of exposure in test electrolytes having aggressive anions have shown the break-down of the passivity (Fig. 5). In the absence and the presence of fluoride ion a limiting stage of the current had been observed (Fig. 6) indicating that a diffusion controlled corrosion process had set in. This clearly indicates that the corrosion product accumulated on the steel surface gets stabilised with the passage of time and is considerably resistant to migration of ions through it. This corroborates the observations recorded in weight-loss studies where the passage of time had brought down the corrosion rate (Table 3). The corrosion rate and the limiting current density values (Table 4) derived from the plots shown in Fig. 6 also confirm the findings of weight-loss studies where the anion resulted in an increase in corrosion rate. A comparison of corrosion rate evaluated by weight-loss and electrochemical techniques (Tables 3 and 4) clearly shows that a vast disparity exists between the two data. The corrosion rate evaluated by the Tafel

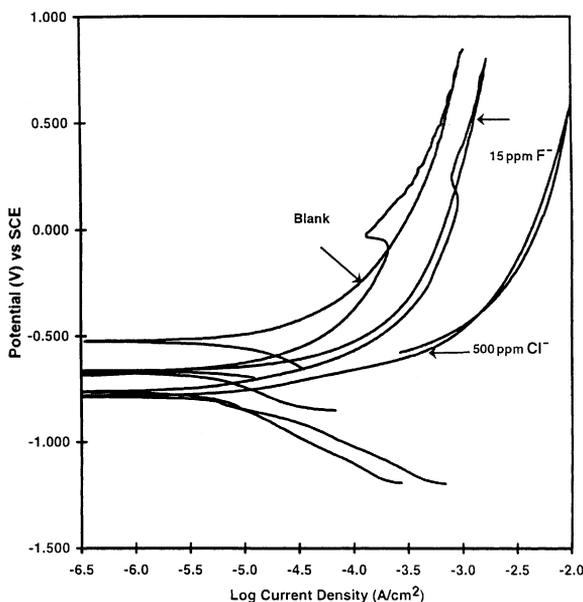


Fig. 6. Cyclic polarisation plots for the steel in 0.01 N NaOH in the absence and the presence of fluoride ion. (The test electrode was exposed for 14 days in solutions prior to running the polarisation study.)

Table 4

Electrochemical parameters of mild steel exposed for 15 days in 0.01 N NaOH having different aggressive anions

Electrolyte	R_p (Ωcm^2)	Limiting anodic current density (A/cm^2)	Corrosion rate ($\mu\text{m}/\text{day}$)
0.01 N NaOH	5.56×10^3	9.51×10^{-4}	0.195
0.01 N NaOH + 15 ppm F^-	3.43×10^3	1.82×10^{-3}	0.245
0.01 N NaOH + 500 ppm Cl^-	1.69×10^3	8.8×10^{-3}	0.498

extrapolation exhibited about five to six times higher corrosion rate than recorded by the weight-loss method (data of 42 days). In contrast to this, the weight-loss data of 10 days of exposure are more closer to the data recorded by the electrochemical technique. In this case, the rate evaluated by the electrochemical method is about two times less in comparison to the rate evaluated by the weight-loss technique. This difference may be attributed to the facts that the electrochemical technique provides an instant rate of corrosion where as the long exposure data is an average of corrosion rate suffered by the steel during the total period of its exposure. Further, the deviation in two data may also be attributed to the various assumptions made in derivation of Stern–Geary equation (Eq. (1)). This equation is derived from the expression [26–28]

$$I_{\text{appl}} = I_{\text{corr}} \left\{ \exp[2.3(E - E_{\text{corr}})/\beta_a] - \exp[-2.3(E - E_{\text{corr}})/\beta_c] \right\} + C(\delta E/\delta t) \quad (2)$$

In the above equation, if $\eta/B < 0.1$, and $C(\delta E/t) = 0$, the relationship becomes linearized and can be written as [29,30]

$$I_{\text{corr}} = \{(\Delta I/2.3\Delta E)(\beta_a\beta_c/\beta_a + \beta_c)\} = 1/2.3R_p(\beta_a\beta_c/\beta_a + \beta_c) \quad (3)$$

In derivation of the above Eq. (3), it is presumed that:

- (a) the open circuit/corrosion potential during the time taken to perform the measurement remains constant;
- (b) the capacitive current i.e. $C(\delta E/\delta t)$ is zero;
- (c) contribution to over potential (η) caused due to solution resistance is negligible.

During the present study, we have tried to minimize the role of factor (a) by allowing the test specimen to remain in contact with the test electrolytes for 16 h. This enabled the potential to get stabilised to the extent of 3.5 mV/h. However, in view of very slow scan rate of potential during the polarisation study, which took several hours for completion of the experiments, the possibilities of change of corrosion potential during the measurements cannot be ruled out. It was not possible to extend the retention time of the specimen in cement slurry beyond 16 h as the slurry started turning in to solid hard mass after this period. This created the problems of damage of glass luggin capillary, specimen and auxiliary electrodes. The effect of second factor as mentioned at (b) above (the role of $C(\delta E/\delta t)$) can be minimized by maintaining very slow scan rate of potential [29,30]. ASTM G59-97 recommends the scan rate of 0.16 mV/s for electrochemical polarisation studies. In the present study, we have gone to 10 times slower rate to generate the data. At such a slow scan rate, although the experiment took considerable period of time for completion, but the double layer capacitance charging effect was expected to be minimum. This factor, if remains active, results in an over estimation of the corrosion rate. The influence of solution resistance (factor c) was minimized by using luggin capillary which was kept very close to the test samples. As such, the effect caused due to this factor is expected to be minimum owing to the highly conducting nature of cement slurry and test solutions having different ions. In view of these extra precautions taken during the experiments, it is therefore, expected that the generated electrochemical data for shorter duration of exposure should be very close to the actual conditions of exposures. The disparity in data generated by the two techniques (weight-loss and electrochemical) should be viewed in context to the above discussion. This disparity, however, in no way affects the conclusions drawn on the role of fluoride induced corrosion of steel in contact of alkaline solutions and embedded in mortars as the experiments in the absence and the presence of fluoride were performed under the identical test conditions.

Since the electrochemical experiments for the steel in contact of cement slurry had indicated that low fluoride ion content has no effect on pits nucleation potential but a strong pitting attack was indicated in 0.01 N NaOH, the need for a more comprehensive study was felt necessary. The steel samples having an artificial pit were, therefore, directly exposed in saturated lime solution +15 ppm F^- for 42 days. A

special precaution was taken to avoid the contamination of the test electrolyte with any other ion. The visual observations were recorded on regular basis. It was observed that no pitting attack took place on steel exposed to lime water having fluoride ion during the initial exposure of 14 days but the propagation of rusting slowly started after this period of exposure from the periphery of pre-pitted surface which slowly spread to whole surface. After 42 days, the samples were gently removed from the test solution, dried at hot plate and then examined by SEM. The corrosion products accumulated at the surface were also characterised by X-ray diffraction (XRD) studies.

Photographs showing the propagation of pit and morphology of corrosion products accumulated near the pit are shown in Fig. 7(a) and (b) respectively. The particles of corrosion product are spherical in nature having considerable degree of interparticle spatial separation (Fig. 7(b)). Another interesting pattern was noted in variation of pitting attack of the specimen from edges (tempered martensitic ring) to core (ferrite–pearlitic zone) of the sample. The attack was more severe on tempered martensitic ring than on the core area of the samples. The microphotographs are shown in Fig. 8(a) and (b). It is to be noted here that due to very severe corrosive attack on specimen, the tempered martensitic structures are not visible in the photograph. However, the polished and etched sample had shown that both the areas as photographed and reported in Fig. 8(a) and (b) were having tempered martensitic and ferritic–pearlitic structures. These observations indicate that the tempered martensitic area is more prone to pitting attack in alkaline solution than the ferrite–pearlite dominated core area of the specimen. A similar behaviour was also reported by Nice and Ueda [31]. XRD analysis showed that the corrosion products were in the mixed form of magnetite, α -FeOOH and Fe_2O_3 . Very feeble peaks of ν -FeOOH were also observed. However, no peak related to fluoride compounds was noted. This was

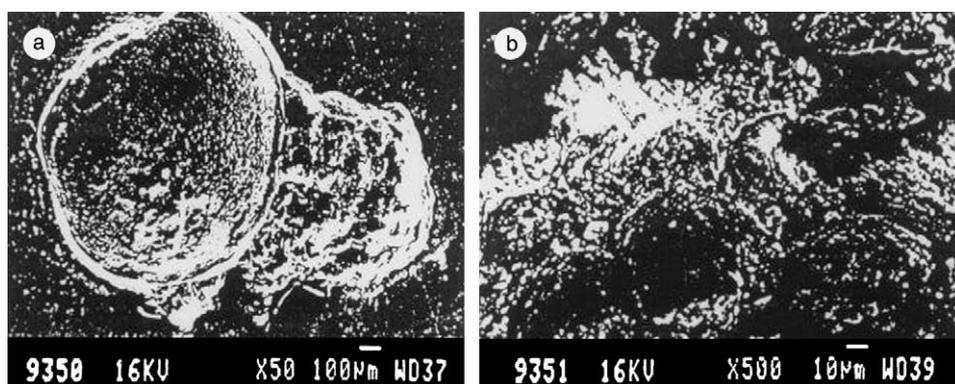


Fig. 7. (a) Propagation of pits on steel surface in the presence of fluoride ions (after the specimen were exposed for 42 days in saturated lime water having fluoride ions). (b) Morphology of corrosion products accumulated in the periphery of the pit (after the specimen were exposed for 42 days in saturated lime water having fluoride ions).

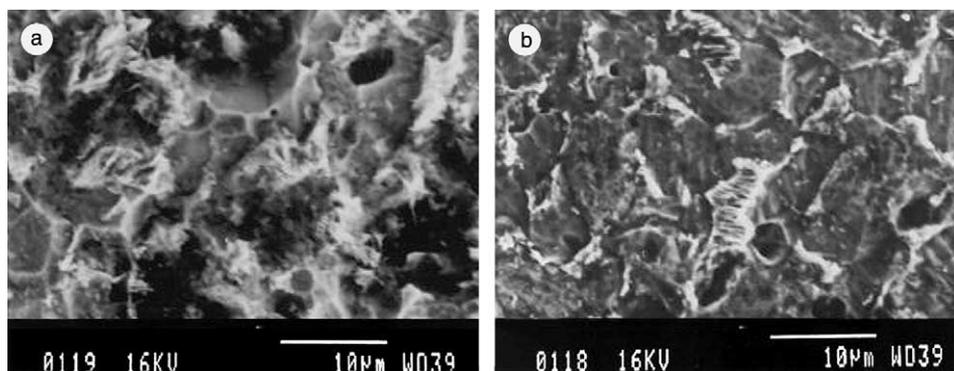


Fig. 8. Preferential attack on tempered martensitic zone of the steel specimen: (a) attack on martensitic structure, (b) attack on pearlitic zone of specimen.

probably due to the limitation of the technique which is unable to identify the minor phases present in corrosion product.

3.1. Corrosive effect of fluoride under different corrosive conditions

As described above, four type of corrodents namely water–cement slurry, mortars contaminated with different ions and exposed in sodium chloride solution, saturated lime solution and 0.01 N NaOH solutions were chosen to determine the corrosive effect of low content of fluoride ion on the steel. In all the cases, the pH varied in the range of 12–13. However, their corrosive effects varied vastly in the absence and the presence of fluoride ion as shown in Table 5. The following observations can be inferred from this table:

- (a) saturated lime water is the most corrosive towards the steel followed by mortar, 0.01 N NaOH and water–cement slurry;
- (b) fluoride has the highest degree of corrosion accelerating effect when present in water–cement slurry and in mortars. It has least effect in aqueous solutions of lime and sodium hydroxide where plenty of soluble oxygen is available in the solution;
- (c) shift in corrosion potential indicates that the fluoride ion has an activating effect on cathodic reaction in aqueous solutions of sodium hydroxide and saturated lime (a positive shift in corrosion potential) where as it has a depolarising effect on anodic reaction of the steel in contact of cement slurry and embedded in mortars (a negative shift of corrosion potential).

The above observations clearly indicate that the mechanism of corrosion of steel is strongly influenced by the fluoride ion depending upon the availability of the oxygen in corrosive environments.

To confirm the above view, experiments were further performed for the corrosion of steel exposed in saturated lime and sodium hydroxide solutions in the absence and

Table 5
Accelerating effect of low content of fluoride ion on corrosion rate of steel exposed in different types of corroding electrolytes, temperature = 30 ± 1 °C

Electrolytes	Control		15 ppm F ⁻		Ratio of corrosion rate in the presence and the absence of fluoride (degree of acceleration)
	Corrosion rate ^a (µm/day)	-E _{corr} ^a (mV) (SCE)	Corrosion rate ^a (µm/day)	-E _{corr} ^a (mV) (SCE)	
Water-cement slurry (after 16 h of exposure of the sample)	0.0035	434	0.0122	549	3.50
Embedded in mortar (after 30 days of exposure of mortars in 3.5% NaCl)	0.01114	622	0.0251	647	2.25
Saturated lime solution (after 16 h of exposure of the sample)	0.0278	468	0.0334	400	1.20
0.01 N NaOH (after 16 h of exposure of the sample)	0.0084	314	0.0111	300	1.33

The corrosion rates were determined by using polarisation resistance technique.

^a Corrosion rate (µm/day) and corrosion potential (E_{corr}) for concentrations of fluoride ion.

in the presence of 15 ppm of fluoride ion at different temperatures. The results on corrosion rate and corrosion potential with rise in temperature are shown in Table 6. The data show that in the absence of fluoride ion, very little effect on corrosion rate of steel is noted with rise in temperature from 30 to 75 °C in both the solutions. This may be attributed to descavenging effects of temperature on dissolved oxygen from the solution and thus having little effect of temperature on the corrosion process. In the presence of fluoride ion, however, the corrosion rate is observed to decrease with increase in temperature in both the electrolytes. The possible mechanism for this behaviour is described in the discussion part of this paper.

4. Discussion

It is general perception that the chloride ion is the most potent in causing localised type of attack on metal surface. Role of this ion on corrosion behaviour of metals has been widely studied owing to their wide spread presence in most type of corrodants. However, amongst the halogens, fluoride ion is expected to be more potent

Table 6

Variation in corrosion rate of mild steel at different temperatures (30–75 °C) in the absence and the presence of fluoride ions

Electrolytes	30 °C		45 °C		60 °C		75 °C	
	Corrosion rate ($\mu\text{m}/\text{day}$)	$-E_{\text{corr}}$ (mV) (SCE)	Corrosion rate ($\mu\text{m}/\text{day}$)	$-E_{\text{corr}}$ (mV) (SCE)	Corrosion rate ($\mu\text{m}/\text{day}$)	$-E_{\text{corr}}$ (mV) (SCE)	Corrosion rate ($\mu\text{m}/\text{day}$)	$-E_{\text{corr}}$ (mV) (SCE)
0.01 N NaOH	0.0193	373	0.0193	373	0.0193	381	0.0206	383
0.01 N NaOH + 15 ppm fluoride	0.0227	342	0.0152	369	0.0129	377	0.0122	375
Saturated lime solution	0.0315	449	0.0271	430	0.0331	409	0.0337	399
Saturated lime solution + 15 ppm fluoride	0.0452	467	0.0303	430	0.0206	413	0.0167	397

All the studies were performed using polarisation resistance technique after exposing the specimen in test electrolytes for 16 h.

in causing the pitting and general corrosion. This is mainly due to its smaller ionic size than the other halogen ions (the ionic size of fluoride and chloride ions are 1.36 and 1.81 Å, respectively) and also due to the presence of very high localised negative charge density on this ion. The ionic size of O_2^- in protective oxides on metals is 1.41 Å [32]. The fluoride ions, therefore, can very easily dislodge the passive layer of oxide from metal surfaces and form soluble complexes with the metal cations resulting in accelerated corrosion attack. This ion, therefore, is expected to have more damaging effect toward metals than the other halides. This is corroborated by the findings recorded in Tables 1 and 7, Fig. 4, where a low concentration of fluoride has more deleterious effect on steel in contact of cement slurry than the equal concentration of chloride ion (the corrosion rate of the steel in cement slurry is found to be double in the presence of 15 ppm fluoride ion (Table 1, 0.012 $\mu\text{m}/\text{day}$) than in the presence of 15 ppm chloride ion (Table 7, 0.0055 $\mu\text{m}/\text{day}$)). Pitting potentials also move in more active direction in the presence of fluoride ion (Fig. 4).

Table 7

Effect of fluoride and chloride ion concentrations on electrochemical parameters and corrosion of steel exposed in water/cement slurry ($w/c = 0.5$)

Concentrations of chloride (ppm)	Corrosion rate ($\mu\text{m}/\text{day}$)	Concentrations of fluoride ion in combination of 500 ppm $\text{Cl}^- + \text{XF}^-$	Corrosion rate ($\mu\text{m}/\text{day}$)
0	0.0035	0	0.0334
15	0.0056	4	0.0556
30	0.0083	6	0.0529
150	0.0111	10	0.0556
500	0.0334	15	0.167

Experiments performed at room temperature after exposing the specimen for 16 h in test electrolytes.

This is evident from the results shown in Figs. 3 and 4 and Table 7 that the exposure of the steel in the cement slurry experiences very low level of corrosion rate even up to 500 ppm of chloride ion (0.033 $\mu\text{m}/\text{day}$) whereas it starts showing the generation of non-passivating type of pits and accelerated corrosion even at the concentration of 10 ppm of fluoride ion. This confirms the preferential interaction of fluoride ion with steel surface in comparison to chloride ions. A similar trend has also been reported by Pryor [33].

Severity of corrosive effect of fluoride ion towards steel in alkaline environment is determined by its concentration and oxygen content in the solution. At very low concentration of fluoride ion, it causes the acceleration of corrosion and induces pitting attack. Its corrosive effect is also accelerated in the presence of dissolved oxygen (Table 6, where a rise in temperature of test electrolyte and hence depletion of oxygen from the test electrolytes has resulted in a decrease of corrosion rate in the presence of fluoride ion). Singh et al. [34] have also reported that the corrosion rate of steel comes down drastically when sodium fluoride solution was saturated with nitrogen. Although no satisfactory explanation is available at the moment but it appears that this is some how related to the solubility of corrosion product formed on the steel surface. In the presence of oxygen, the Fe^{2+} ionised from the steel surface is quickly converted to Fe^{3+} which combines with fluoride ion to form poorly protective Fe_2O_3 and FeF_3 film [1]. This explanation gets further support from the findings of Zotikov et al. [5], who reported that the corrosion rate of steel in NH_4F solution increased when dichromate ions (a strong oxidizer) were added in the fluoride solution. They had further reported that the corrosion rate of steel decreased with concentration of the test solution which was attributed to the fact that the solubility of oxygen in the concentrated solution becomes low and fluoride ion forms protective and difficult to dissolve FeF_2 film (solubility product = 1.46×10^{-10}). In order to confirm the above reasoning further, we had determined the corrosion rate of the steel in sodium hydroxide solution having tartrate and fluoride ions. Mayne and Turgoose [35], have shown that the tartrate ions in 0.1 M NaOH solution have an inhibition effect on thickening of oxide film on steel surface. This is due to the tendency of tartrates to form complex with $\text{Fe}(\text{OH})^+$ which in its uncomplexed state oxidises to form Fe_2O_3 . In the presence of fluoride ions, tartrate ions, therefore, are expected to inhibit the formation of Fe_2O_3 and rather help in the formation of FeF_2 as corrosion product. Our results corroborate this hypothesis as shown in Table 8. It is noted from this table that the fluoride ion which accelerates the corrosion in the absence of tartrate ions has an inhibiting effect in its presence. Further, the shift of corrosion potential in nobler direction indicates that the reaction is being stifled due to the formation of protective film on the surface. The results of this Table further provide a very important indication that the fluoride induced corrosion of steel in alkaline environments can be effectively controlled by blending tartrate ions in the solution. A study to this effect is in progress by us and will be published shortly.

The results of Table 3 clearly demonstrated that the accelerating effect of fluoride ion is less in the presence of excess of Ca^{2+} in the solution, in comparison to in the presence of Na^+ ions. This observation is in agreement with the findings of Macias and Escudero [14,15] who reported that the fluoride induced corrosion of steel is

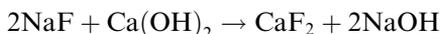
Table 8

Role of tartrate ions on corrosion rate of the steel in the absence and the presence of fluoride ion added in 0.1 N NaOH solution, temperature of the bath = 30 ± 1 °C

Type of ions in the base electrolyte	Corrosion rate ($\mu\text{m}/\text{day}$)	–Corrosion potential (mV, SCE)
Blank	0.0981	459
15 ppm F^-	0.1127	472
50 ppm tartrate	0.1085	501
50 ppm tartrate + 15 ppm F^-	0.0709	480
50 ppm tartrate + 50 ppm F^-	0.0692	447
100 ppm tartrate + 50 ppm F^-	0.0417	414

Tests performed after exposing the specimen for 16 h in test electrolytes.

diminished in the presence of excess of Ca^{2+} in the solution. They have attributed it to the formation of poorly ionisable and sparingly soluble CaF_2 salt on the surface of the steel. The cyclic polarisation tests conducted by us for the steel embedded in fluoride containing cement–water slurry and lime water also corroborated the findings of these authors. According to them the fluoride ion from sodium fluoride salt in aqueous phase combines with Ca^{2+} ions generated from the lime, to form sparingly soluble CaF_2 .



The above reaction produces strong alkali (NaOH) which results in an increase of pH of the test electrolyte. This increase in pH may affect the type of film formed on the steel surface. Although the above reasoning of decrease in corrosion rate in the presence of very high concentration of Ca^{2+} and fluoride ions appears quite convincing, nonetheless, the solubility factor of CaF_2 appears to have more decisive role in controlling kinetics of corrosion process. Unlike the other fluoride salts of alkaline earth metals, calcium fluoride possesses lowest solubility in aqueous solutions. This is because of the combination of unusually small size of fluoride ions relative to the large Ca^{2+} ions which results in higher lattice energy of CaF_2 and making the crystal of the salt difficult to dissolve [36]. Another reason for very poor solubility of fluorides of calcium is its inability to form fluoro complexes with calcium cations [37].

It is established beyond doubt by the present study as well as by the previous researchers that fluoride ions in contact of excess of Ca^{2+} ions have an inhibitive effect on general corrosion of steel in alkaline solution but at the same time they have strong pitting tendency towards the metal. An actual exposure test of specimen in saturated lime water having fluoride ions for 42 days has confirmed these inferences. In this case very severe pitting on the steel surface has been noted (Fig. 7(a)). These observations indicate that although F^- has no tendency to initiate instant pitting on the steel surface but accelerates it once entrapped with rust. Mayer et al. [20] have reported the entrapping of fluoride in the scale formed on water side surface of boilers where fluoride content of 800–4000 ppm was observed even when the concentration of fluorides in the boiler water was less than 0.01 ppm. Such entrapping of

fluoride results in the formation of porous and unprotective magnetite film on the steel surface. Cinman et al. [38] have indeed reported that the fluoride ions enter the oxide lattice of metals and replace some of the O_2^- anions of the oxide.

In a freshly prepared water–cement slurry and in mortars, the presence of fluoride ion in the accelerating range (≤ 25 ppm) has greater corrosion accelerating effect (Table 5) than that observed in aqueous alkaline solutions. This may be explained by considering the fact that in aqueous alkaline solutions, the corrosion rate of steel is cathodically controlled and depends upon the availability of oxygen in the solution. The rebars embedded in the concrete, on the other hand, corrode under anodic control and the corrosion product formed on the steel surface plays vital role on the kinetics of corrosion. Due to the presence of very low concentration of fluoride ion in the vicinity of the embedded rebar, FeF_3 type of soluble corrosion product is expected to form which may have an autocatalytic effect on the corrosion of steel. In such a situation, Fe^{3+} will act as a potent cathodic depolariser of corrosion reaction. Further, the availability of free Ca^{2+} in solidified concrete is also doubtful. The formation of sparingly soluble CaF_2 salt in significant amount at the metal surface, therefore, is ruled out as the major part of pore solution of concrete is expected to be present as $NaOH/KOH$ instead of $Ca(OH)_2$ [23–25]. Moreover, the calcium ion is also expected to be masked as $CaSO_4$ and other insoluble phases such as calcium chloro aluminate and ettringite [39–41]. The risk of localized and accelerated general corrosion in the presence of low concentration of fluoride in concrete, therefore, cannot be ruled out in view of the above observations. A more detail study on the role of low content of fluoride ion on rebars embedded in mortar is under progress and will be reported in our next communications.

5. Conclusions

- (a) Presence of low content of fluoride (<25 ppm) has an accelerating effect on corrosion and pitting attack of mild steel in saturated lime water. Above this concentration, it has a gradual inhibitive effect.
- (b) Same trend as stated at (a) above is also noted for the steel embedded in concrete mortars and exposed to water–cement slurry.
- (c) Fluoride has more synergistic deteriorating effect on steel's corrosion in combination with chloride derived from sodium than from calcium salt, especially at higher content of the fluoride.
- (d) Tempered martensitic structure is more prone to pitting attack than ferritic–pearlitic structures in alkaline solution having fluoride ion.
- (e) Electrochemical polarisation studies have shown that the low content of fluoride in saturated lime solution accelerates the corrosion rate by cathodic depolarisation where as at its higher concentrations (≥ 25 ppm) it inhibits the reaction due to the anodic polarisation process.
- (f) The studies indicate that there exists the possibilities of accelerated corrosion and pitting attack on embedded steel bars if low content of fluoride is available on the steel surface.

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