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CORROSION OF REINFORCING STEEL IN MORTAR OF CEMENT WITH CaF_2 AS A MINOR COMPONENT

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ABSTRACT

This paper reports on the corrosion behaviour of steel embedded in mortar of cement manufactured using CaF_2 as a mineraliser and flux agent. Corrosion rates of steel in this new cement measured with electrochemical techniques are compared with the corrosion rates of steel in contact with a traditional cement of similar characteristics in the same conditions. It was confirmed that the new cement does not lead to pitting corrosion and corrosion rates of steel are similar to traditional cement even in presence of corrosive agents such as chlorides or carbonation of cement.

INTRODUCTION

Fluoride can be present as a minor component in low-energy cements. One of the ways of decreasing the energy consumption in cement manufacture is the use of fluxes and mineralisers (1) and CaF_2 acts both as a mineralizer and as a flux in promoting the formation of alite (2)(3). The burning temperature for production of Portland cement clinker can be decreased by about 150°C (4), but opinions have differed as to the energy saving thereby obtainable (5)(6).

Corrosion of steel in concrete has become over recent years an increasingly important factor when considering the maintenance of buildings and structures and the effects produced by fluoride presence in modern cements have to be analyzed in order to make correct predictions of service life.

In a previous paper (7), the authors describe the modifications that the presence of fluoride has on the corrosion behaviour of reinforcing corrugated steel bars in alkaline solutions used to simulate the aqueous phase present in concrete pores, that is, a saturated solution of $Ca(OH)_2$ with addition of NaF in different proportions from 0,1 to 1 M. The results obtained in this medium are compared with the results obtained in 0.04 M NaOH solutions which has similar pH to $Ca(OH)_2$ saturated solution. This paper also analyses the joint presence of chlorides and fluorides effects. Results show that fluoride anions are able to produce pitting of reinforced steel in alkaline media of high pH but pitting potential values are more positive than those found in presence of chloride anions under comparable concentration and experimental conditions. In $Ca(OH)_2$ saturated solution, the precipitation of CaF_2 lowers F^- concentration below the minimum that promotes a pitting corrosion process. The presence of fluoride in these media causes an increase in passive film dissolution and consistently in corrosion rates of reinforced steel with fluoride concentration.

This paper reports a study of the corrosion behaviour of reinforced steel in mortar made with a cement manufactured using CaF_2 in its clinkerization process according to a patented procedure (8). Corrosion rates are compared with those obtained in a cement of the same characteristic but made traditionally in the same factory. The corrosion behaviour has been compared in mortars without any addition, in mortar contaminated by NaCl and in mortars submitted to a process of accelerated carbonation.

EXPERIMENTAL

Materials and Procedure

Reinforcing corrugated 6 mm nominal diameter and 8 cm long steel bars with an exposed area of 5.6 cm^2, were used.

Cements used were: cement A, a normal white cement and Cement B, a white cement manufactured with CaF_2. The potential composition of the clinkers and chemical analysis of these cements are presented in Table I and Table II.

Mortars specimens of 8 × 5.5 × 2 cm with w/c = 0.5 and c/s = 1/3 were made. Two mild steel rods and a central carbon bar - counter electrode - were cast in the mortar prims as can be seen in Fig. 1 a). A saturated calomel electrode was used as reference. One third of these specimens were made with 2% of NaCl by weight of cement.

TABLE I
Potential Mineralogic Composition of Clinkers

SAMPLE	C_3S_{ss}	C_2S_{ss}	C_3A	C_4AF	FL*
A	71%	9.6%	14.7%	1%	-
B	61%	23.5%	4.8%	0.7%	9%

Standard mineral nomenclature for cements: $C = CaO$, $A = Al_2O_3$, $S = SiO_2$, $F = Fe_2O_3$
FL*= Fluorellesteadite ($3\ C_2S \cdot 3\ CaSO_4 \cdot CaF_2$)

TABLE II
Chemical Analysis of Cements

SAMPLE	LOI	SiO_2	Al_2O_3	CaO	Fe_2O_3	MgO	Na_2O	K_2O	SO_3	CaF_2
A	3.98	21.28	3.92	66.05	0.29	0.83	0.05	0.16	3.23	0.59
B	0.82	24.34	1.98	67.60	0.37	0.55	0.05	0.10	2.78	1.65

The specimens were cured during 24 hours in humidity saturated atmoshere and afterwards kept for 83 days in a chamber at 50% or 100% R.H. Then the samples at 50% R.H. were partially immersed (P.I.) in distilled water in individual polyethylene bottles (see Fig. 1 b)). Samples kept at 100% were totally immersed (T.I.). In the case of specimens with 2% NaCl addition, the total or partial immersion was in natural sea water.

Once again the steel has get a passivated state (after 13 days), one series of the specimens without any addition was taken out of the chambers at 50 % or 100 % R.H. and rapidly carbonated in CO_2 atmosphere during 11 days. Then the specimens were put again in the previous R.H. conditions.

Techniques Used

Tafel potentiodynamic polarization curves from rest potential to ± 250 mV at a scanning rate of 60 mV/min were performed using a PARC potentiostat.

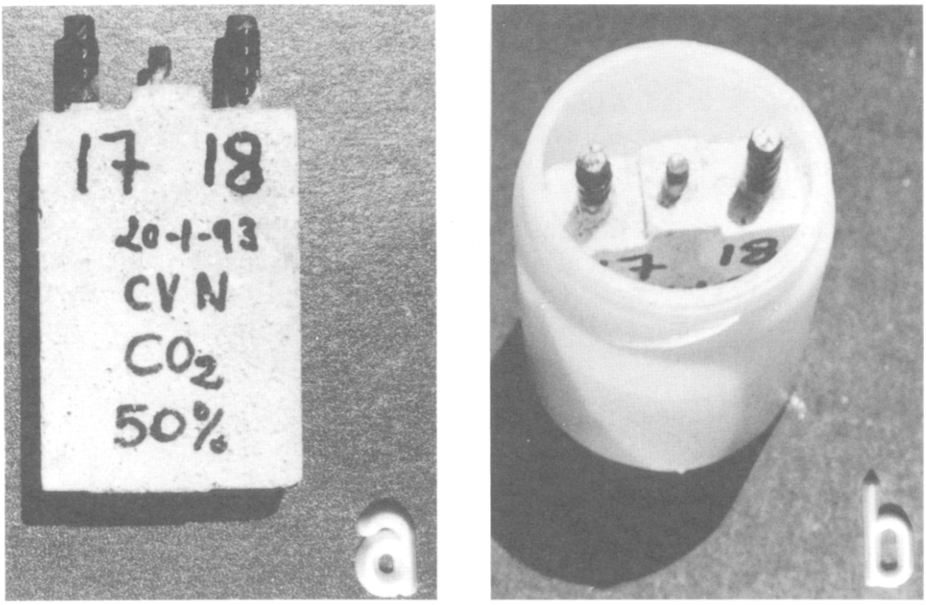

FIG. 1
a) View of mortar/rebar specimen. b) Specimen partially immersed.

The polarization resistance measurements were carried out by means of an AMEL potentiostat. Rp was estimated by the ratio between applied polarization (10 mV when the steel is actively corroding and 30 mV when is passivated) and the current response measured after a time stabilization of about 30 seconds.

The corrosion intensity was evaluated applying the Stern and Geary formula (9)(10):

$$i_{corr} = \frac{B}{R_p}$$

$$B = \frac{\beta_a \cdot \beta_c}{2.3(\beta_a + \beta_c)}$$

The value of constant B was deduced from the experimental results of polarization curves drawn.

EXPERIMENTAL RESULTS

Tafel Polarization Curves

Tafel polarization curves were drawn only at the end of the experiments to minimized any alteration of the electrodes. This is the reason way they were only obtained in conditions of total or partial immersion.

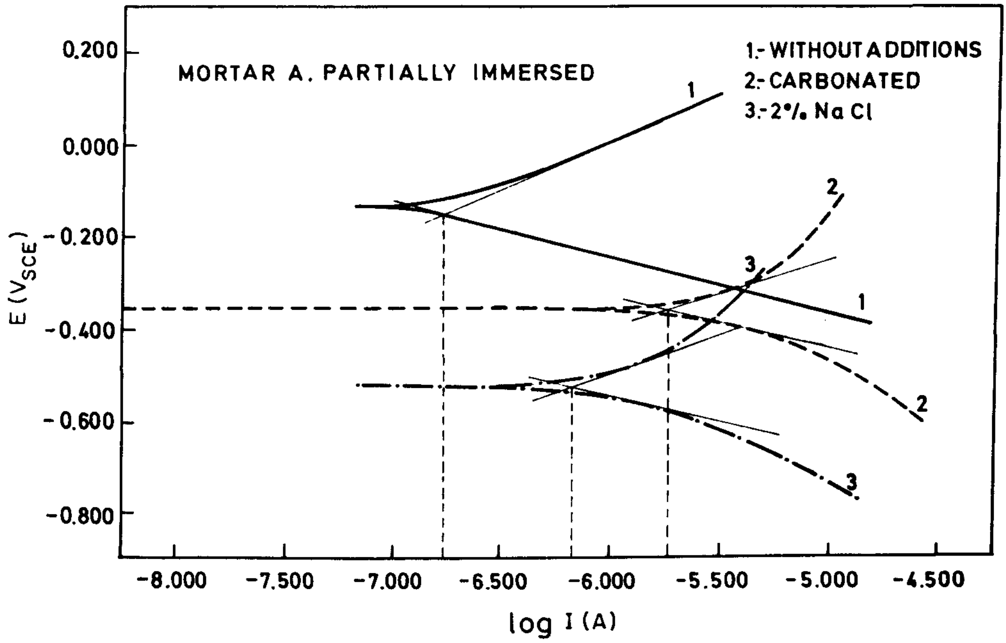

FIG. 2

Potentiodynamic Polarization E-logi curves drawn at 60mV/min for steel in mortar A partially immersed.

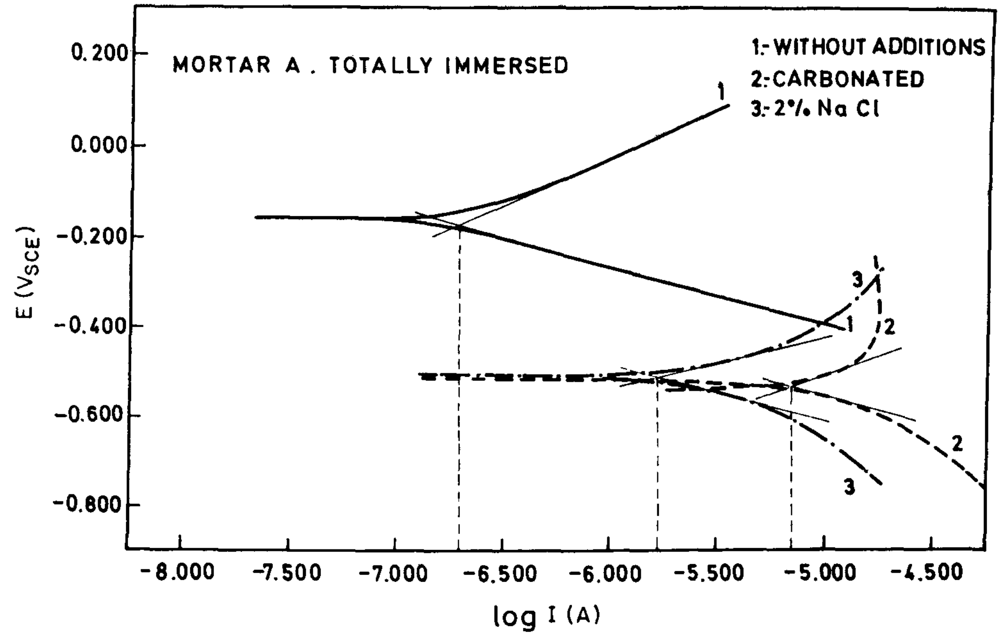

FIG. 3
Potentiodynamic Polarization E-logi curves drawn at 60mV/min for steel in mortar A totally immersed.

Figures 2 to 5 show the potentiodynamic polarization E-logi curves drawn at 60mV/min for steel in mortars A or B with and without 2% NaCl addition and carbonated in both conditions, total and partial immersion.

Table III contains values of Tafel slopes, β_a and β_c, and corrosion rates obtained from those Tafel polarization curves. The values of Stern and Geary's formula, B, calculated with those of Tafel slopes and the simultaneous registered corrosion rates from polarization resistance measurements are also presented.

The values of anodic and cathodic Tafel slopes are about 100 mV/dec when corrosion rate of metal is higher than 0.1 μA/cm^2. When i_{corr}< 0.1 μA/cm^2, cathodic Tafel slopes are also about 100 mV/dec but anodic ones are above 200 mV/dec, that means that the corrosion process is under anodic control due to the passivation film generated on the electrode surface.

The values of Stern and Geary's formula, B, calculated with Tafel slopes values are: a medium B value of 24 mV when the metal is actively corroded and a medium B value of 37 mV when is in a passive state. Table III also shows the good correlation between corrosion rates simultaneously measured with R_p and Tafel polarization curves.

Corrosion Rate Determination

The i_{corr} and E_{corr} values of steel bars embedded in mortar A and B without any addition, carbonated and mixed with 2 % NaCl are represented versus time in Figures 6 to 8. In

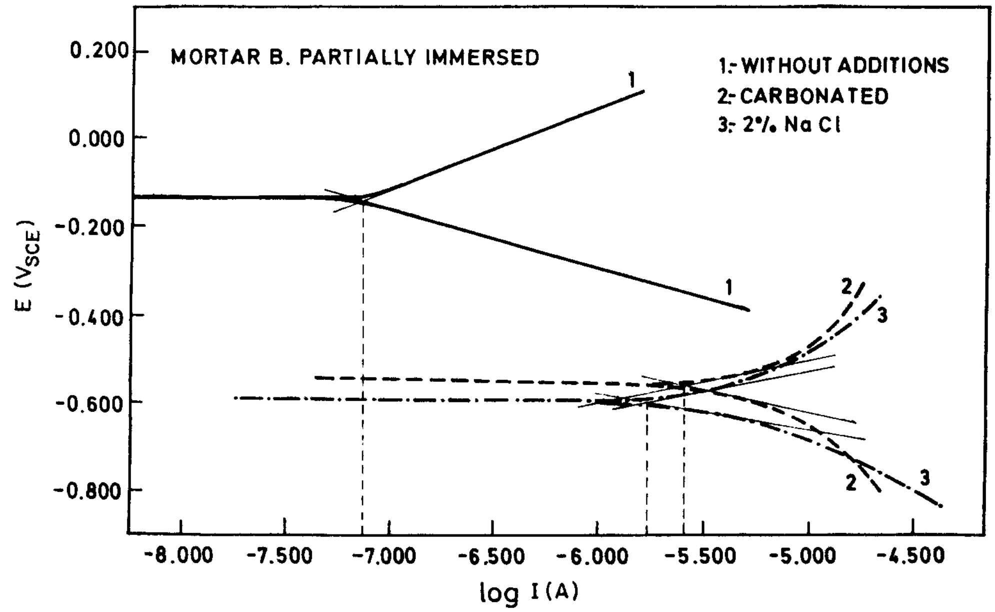

FIG. 4
Potentiodynamic Polarization E-logi curves drawn at 60mV/min for steel in mortar B partially immersed.

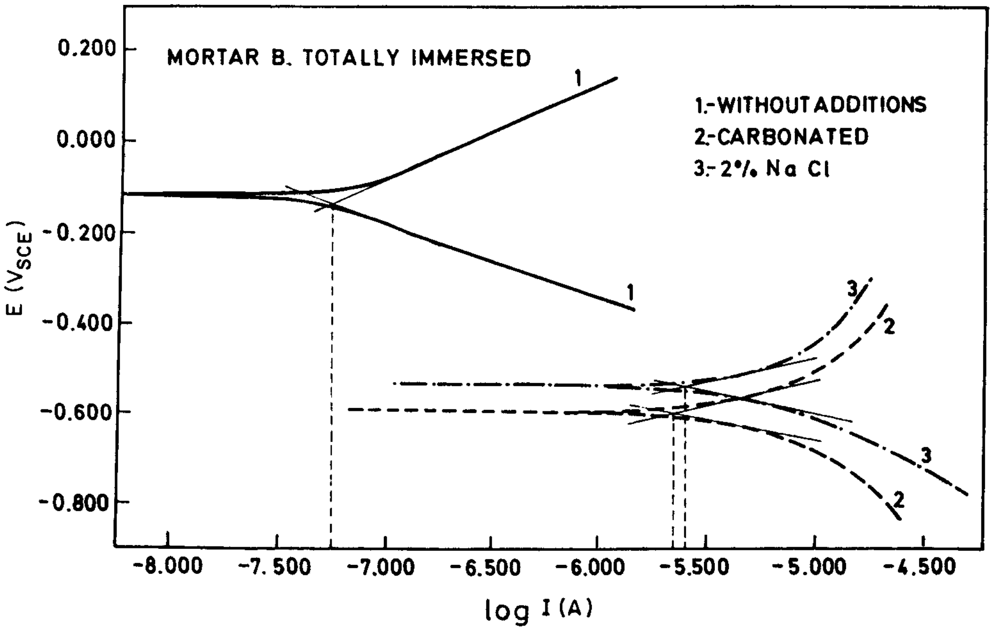

FIG. 5
Potentiodynamic Polarization E-logi curves drawn at 60mV/min for steel in mortar B totally immersed.

Table III
Values of Tafel Slopes and Corrosion Rates Obtained from Tafel Polarization Curves

Sample	R.H.	Polarization curves				R_p
		β_a (mV/dec)	β_c (mV/dec)	B (mV)	i_{corr} (μA/cm^2)	i_{corr} (μA/cm^2)
A	P.I.	205	116	32	0.025	0.012
A	T.I.	207	129	34	0.028	0.012
A+ CO_2	P.I.	136	94	24	0.481	0.567
A+ CO_2	T.I.	123	106	25	0.365	0.430
A +2%NaCl	P.I.	116	102	24	0.145	0.089
A +2%NaCl	T.I.	107	121	24	0.289	0.288
B	P.I.	193	129	34	0.011	0.010
B	T.I.	228	140	38	0.012	0.011
B + CO_2	P.I.	100	94	21	0.364	0.581
B + CO_2	T.I.	91	87	19	0.290	0.465
B +2%NaCl	P.I.	154	98	26	0.561	0.415
B +2%NaCl	T.I.	161	114	29	0.429	0.647

these figures it could be seen that, initially i_{corr} values are around 0.1 μA/cm^2 and E_{corr} about -400 mV for all samples.

For mortars A and B without any addition, after one week, i_{corr} values are below 0.02 μA/cm^2 and E_{corr} about -150 mV. These values indicates the passivation of steel. The change in the environmental conditions to a higher relative humidity, influences directly the resistivity of the mortar which decreases drastically. However, there is only a light increase in corrosion rates; i_{corr} values keep under 0.2 μA/cm^2 until the end of the test. This corrosion rates lead to a material loss of 116 μm in 50 years.

In Fig. 7 could be seen that when the mortars are carbonated, the passivation state is destroyed by the decrease in pH of the pore phase. Accordingly, steel stars to corrodes with a corrosion rate higher than 0.1 μA/cm^2 and E_{corr} values moves simultaneously to more negative ones.

On the other hand, the calcium carbonate precipitated in the mortar pores as a consequence of the reaction between the calcium hydroxide and the CO_2, decreases the porosity of the material and increases its resistivity. In these conditions, the corrosion process is under resistivity control. This fact justifies the gradual decrease of corrosion rate registered after carbonation of samples and the lowers i_{corr} for samples at 50 % R.H. compared with those at 100 % R.H..

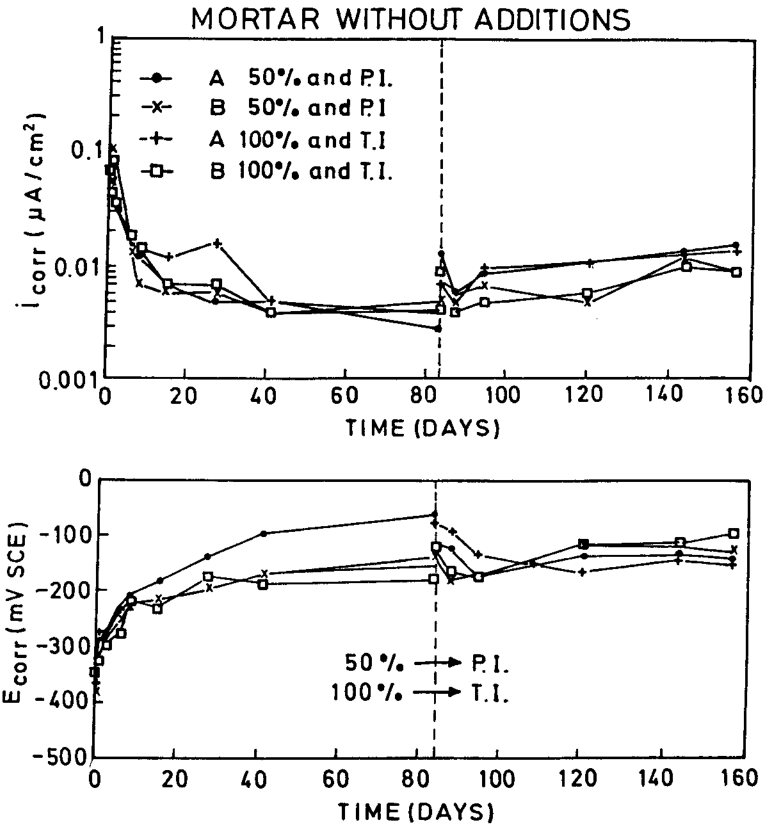

FIG. 6

i_{corr} and E_{corr} values versus time for steel bars embedded in mortars A and B.

When the environmental conditions change to partial or total immersion, the resistivity of the mortars diminish considerably and i_{corr} increases to values around to 0.5 μA/cm² that remain constant until the end of the test. Those corrosion rates means a material loss of 5.8 μm/year.

The results presented in Fig. 8 show that an addition of 2 % of NaCl to the mix water is not enough to promotes a pitting corrosion of steel embedded in mortar A or B. The corrosion rates measured are only slightly higher than those measured in mortars without any addition in the same condition.

To increase the aggressiveness of the conditions tested in order to magnified the possible different behaviour of mortars A and B, the total or partial immersion of these samples was in natural sea water. The present of higher chloride concentration leads to corrosion rates about 0.5 μA/cm². Again corrosion behaviour of steel embedded in both cements is similar.

DISCUSSION

The final corrosion rates of steel embedded in mortars A and B in all the conditions tested

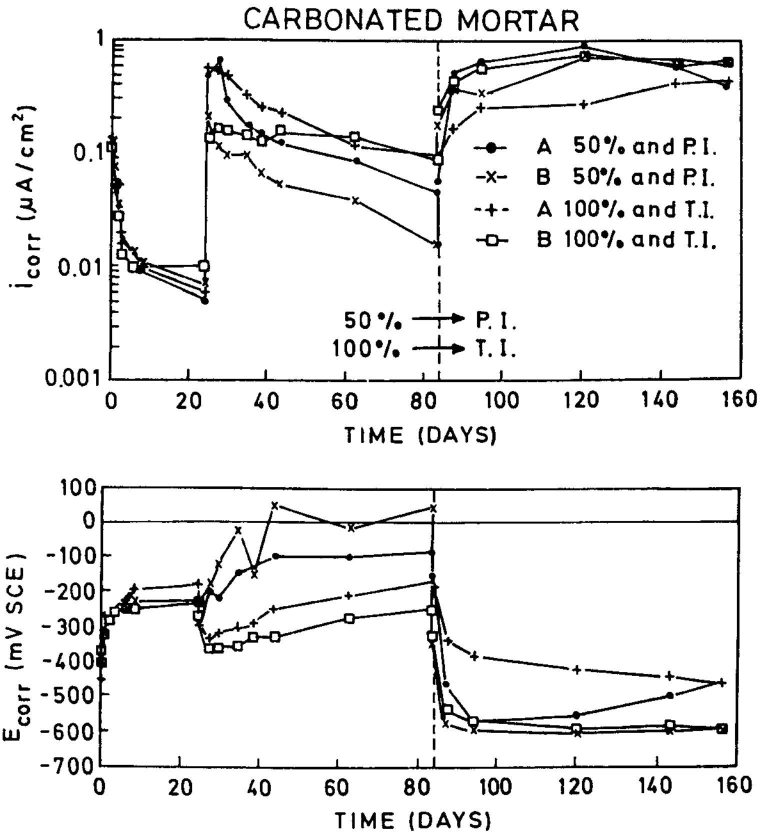

FIG. 7

i_{corr} and E_{corr} values versus time for steel bars embedded in mortars A and B carbonated.

are reported in Figure 9 in order to summarized the results obtained in the present paper. Nevertheless that is a punctual date, it is representative of the corrosion tendency of steel in each condition. From these Figures it can be drawn the following conclusions:

- Both mortars of cement A and B without any addition guarantee the passivity of reinforced steel in whatever condition of exposure. Corrosion rates measured are very low and similar for both cements.

- The carbonation of mortars A and B leads to destruction of passivity of steel which starts to corroded at a corrosion rate function of the resistivity of the mortar. Samples of cement A in 50 % R.H. environment present lowers corrosion rates due to its higher resistivity.

- In presence of chlorides corrosion rates of steel embedded in mortar B are slightly higher than those of mortar A that can be due to the different bond chloride capacity of both cements. Cement A has a C_3A content three times higher than cement B.

Therefore, results of the present work indicate that corrosion rates of reinforcing corrugated steel bars embedded in mortar of the new cement B manufactured adding CaF_2

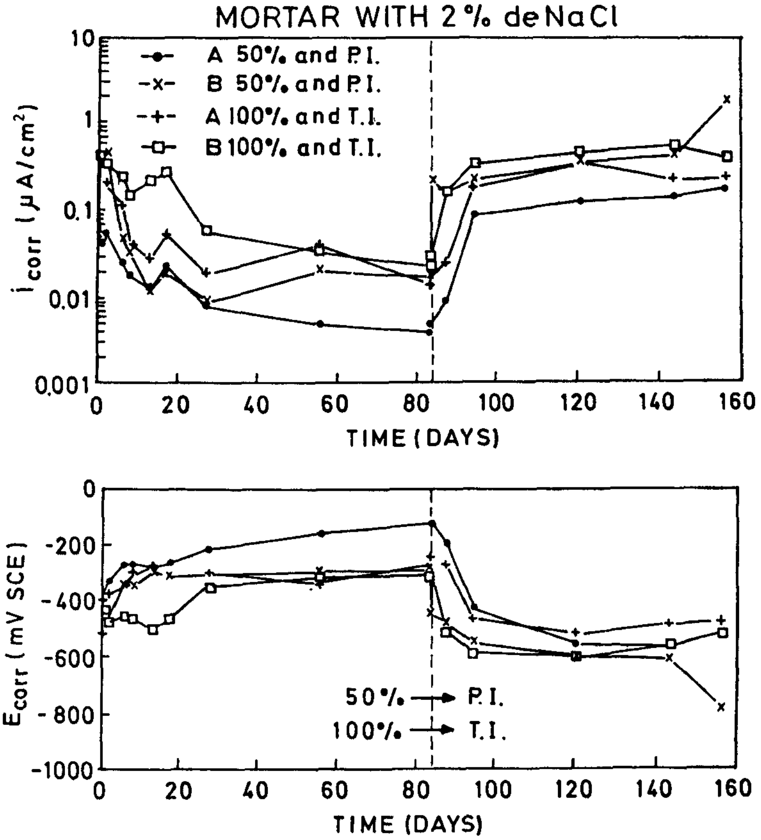

FIG. 8

i_{corr} and E_{corr} values versus time for steel bars embedded in mortars A and B with 2% NaCl.

are similar to corrosion rates measured for a traditional made cement A. The corrosion behaviour of cement B agrees with previous conclusions inferred from concrete liquid phase simulating solutions test (7). According to these, fluoride ions precipitated as CaF_2 in a $Ca(OH)_2$ saturated media. The low solubility of this product lowers fluoride concentration bellow the minimum needed to promotes a pitting corrosion of steel, but the presence of fluoride in solution causes an increase in passive film dissolution and corrosion rates. This increase in corrosion rates has not been detected in steel embedded in mortar B due to the very low concentration of F^- in the pore phase of this mortar. Fluoride added to the cement clinker could be lost by volatilization at temperatures above 1050 °C or gets into the clinker phases. Thus, the presence of a F-apatite (ellestadite) phase was detected by X-ray diffraction in cement B mineralogical composition. Both process collaborated to lowers fluoride concentration in pore phase.

CONCLUSIONS

-Corrosion behaviour of reinforced steel embedded in mortar of cement manufactured employing fluorides to lower the clinkering temperature, is similar to that of cement traditionally made.

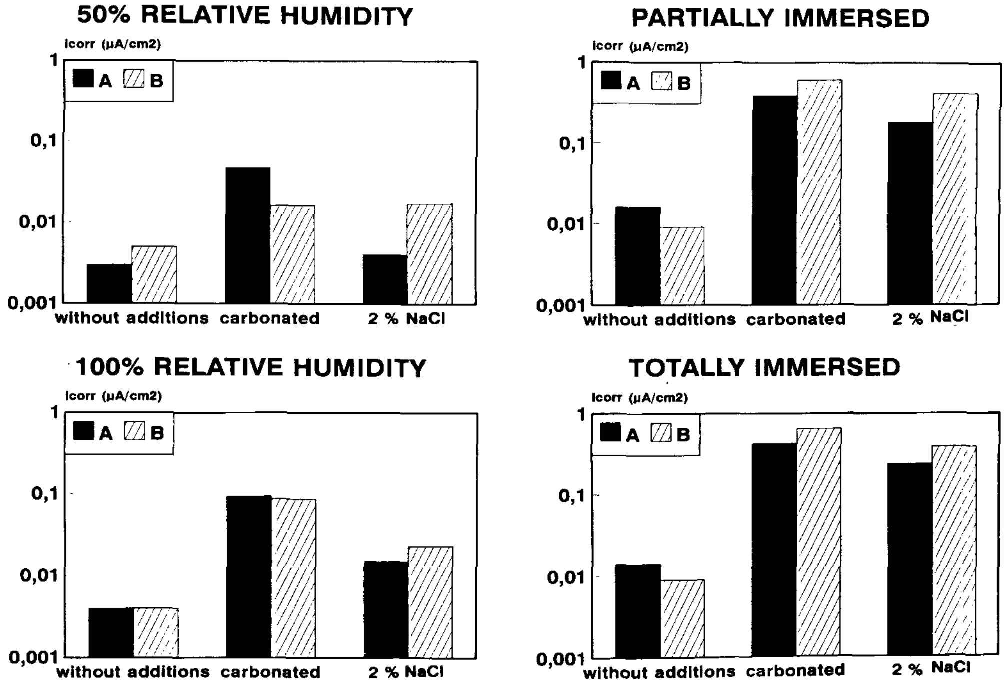

FIG. 9
Final corrosion rates of steel embedded in mortars A and B in all the conditions tested.

-Fluoride concentration in the pore phase of this cement is not hight enough to promote a pitting corrosion or to increase significantly the corrosion rate of steel.

-In presence of corrosion causes agents as chlorides or carbonation of cement is not necessary any additional corrosion protection method when the reinforcements are in contact with this type of cement.

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